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16. ABSTRACT The proceedings document presentations at the Symposium on Iron and Steel Pollution Abatement Technology for 1983, the fifth in this series, held in Chicago on October 18-20, 1983. It provided a forum for the exchange of information on technological problems related to multimedia pollution control in the iron and steel industry. American and international representatives from industry, academia, the research community, public interest organizations, and federal and state governments participated. Session 1 dealt with water pollution abatement, Session 2 with air pollution abatement, and Session 3 with RCRA and multimedia pollution abatement. Because of its interest, one paper (Appendix A) is included although it was not presented at the symposium.

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ABSTRACT

This report documents presentations at the Symposium on Iron and Steel Pollution Abatement Technology, Chicago, IL, October 18-20, 1983. The symposium provided a forum for the exchange of information on technology problems relating water, air, and multimedia pollution abatement in the iron and steel industry.

The traditional opening session was eliminated, providing maximum opportunity for the exchange of technical information. Session 1 consisted of 10 papers on water pollution abatement. Session 2 consisted of 11 papers on air pollution abatement. Session 3, consisting of seven papers, concentrated on multimedia pollution abatement and ramifications of the Resource Conservation and Recovery Act (RCRA). The 29th paper included in the proceedings, although not presented, had to do with the simultaneous removal of organics and ammonia .

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OPENING REMARKS

John S. Ruppersberger
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Good morning. Welcome to the fifth symposium on iron and steel pollution abatement technology.

I'm John Ruppersberger of EPA's Office of Research and Development.

The object of the symposium is to present current technical information of interest. The papers represent the views of their authors.

You are encouraged to participate in the discussion at the end of the paper if you have a technical question or comment.

The program is particularly strong due to the very good response to the call for papers. The opening session included in previous symposia has been eliminated to provide more time for the regular technical program.

I'd like to introduce Charles W. Askins, who shares the responsibilities of General Chairman with me.

Chuck is Group Manager of Environmental Control of Babcock and Wilcox's Tubular Products Group.

SESSION 1

WATER POLLUTION ABATEMENT

CHAIRMEN:

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and

Edward L. Dulaney
Effluent Guidelines Division
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Washington, DC 20460

DEVELOPMENT OF SCREENING TESTS FOR EVALUATING THE DEWATERING OF HOT-ROLLING SLUDGES

by: P. H. Damon and D. E. Hassick
United States Steel Corporation
Research Laboratory
125 Jamison Lane
Monroeville, PA 15146

ABSTRACT

Solids removed from water in steel-mill wastewater-treatment systems are in the form of sludges that must be dewatered and disposed of. Properties of these sludges vary widely, depending on the mill processes from which the wastewaters originated. Sludge from hot-rolling mills, with its relatively high oil content and specific gravity, is a difficult material to dewater.

U. S. Steel conducted laboratory studies to evaluate the effectiveness of three basic types of filtration (i.e., vacuum, belt press, and pressure) for dewatering hot-rolling sludges. Vacuum filtration testing was readily accomplished by the use of a vacuum filter-leaf apparatus. However, no standard laboratory belt- or pressure-filtration simulator were readily available, so small units had to be developed. A belt-press simulator was constructed by modifying a Carver static hydraulic press. The pressure-filtration simulator was a specially fabricated vessel with the capability of simulating both conventional and diaphragm-assisted recessed-plate filtration.

After operating procedures were developed, the simulators were used to measure dewaterability of hot-rolling sludges from hot-strip, primary/bar, slab/plate, and structural mills. The addition of polymer was required for successful belt-press simulation and addition of lime enhanced filter press simulator operation. Rigid filter cakes were generated in both units which in most cases appeared firm enough for landfilling. In comparative tests with commercial-size belt and pressure filters, the dewatering performance of both simulators correlated satisfactorily (based on cake solids content) with the larger equipment. The pressure-filtration simulator can also be utilized to predict the dewatering rate of a full-scale unit.

These units were demonstrated to be viable simulators for dewatering hot-rolling sludges by belt and filter presses and can be utilized as screening devices for indicating where further testing by pilot-scale units is warranted.

BACKGROUND AND INTRODUCTION

Sludge dewatering has become an increasingly critical problem in the American steel industry as the need for economic disposal and/or reuse of solid wastes increases. An estimated 3-million metric tons of waste sludge are generated annually,[1)*] with about half of this amount available for reuse. Rolling mills account for about 300,000 metric tons of sludge annually, virtually all of which must be landfilled and cannot be reused in its existing state. As Federal legislation makes landfilling increasingly expensive, sludge-dewatering costs become an increasingly important consideration. Processes for dewatering sludges at lower cost by eliminating the need for thermal drying, with its attendant high energy consumption, are needed today.

U. S. Steel has recognized this immediate need for efforts to enhance the dewaterability of sludges in both existing steelmaking facilities and in new treatment plants being designed. Hot-rolling-mill sludge, with its relatively high oil content and specific gravity, is a very difficult sludge to dewater. Accordingly, U. S. Steel undertook a program to (1) investigate properties of sludges from various hot-rolling-mill operations, and (2) develop techniques to establish methodology that would allow prediction of performance of candidate dewatering systems. Screening tests were developed for evaluating the dewatering of rolling-mill sludges, and are the topic of this paper.

Figure 1 illustrates a typical rolling-mill wastewater treatment and recycle system requiring solids-liquid separation processes, such as sedimentation basins, clarifiers, thickeners, lagoons, or multimedia filters. Sludges from these sources were used in the study.

Vacuum filtration (Figure 2) has been a time-tested method of dewatering many sludges and has proven particularly effective for those from blast furnaces and basic oxygen furnaces. For other types of sludges such as hot-rolling mills, vacuum filters have had wide use but often with serious limitations in dewatering the sludges. Two alternative types of equipment being considered in these applications are belt-press filters and filter presses. In a belt-press filter, sludge is squeezed between two filter belts by sets of rollers that exert increasing pressure as the sludge passes though the unit (Figure 3). In a filter press the sludge is squeezed, in chambers usually aligned vertically, under pressures as high as 280 psi (Figure 4).

Literature reviews verified the lack of any fully established or commercially available type of laboratory simulator for belt presses and filter presses. Laboratory evaluations demonstrated the inadequacy of simple dewatering methods such as "capillary suction time" or Buchner funnel tests to predict cake solids characteristics necessary to determine the best type of filter. What was needed were small laboratory-scale devices to accomplish this, similar in function to the vacuum filter leaf test apparatus which has become a standard unit for vacuum filtration simulation (Figure 5). This

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* See References.

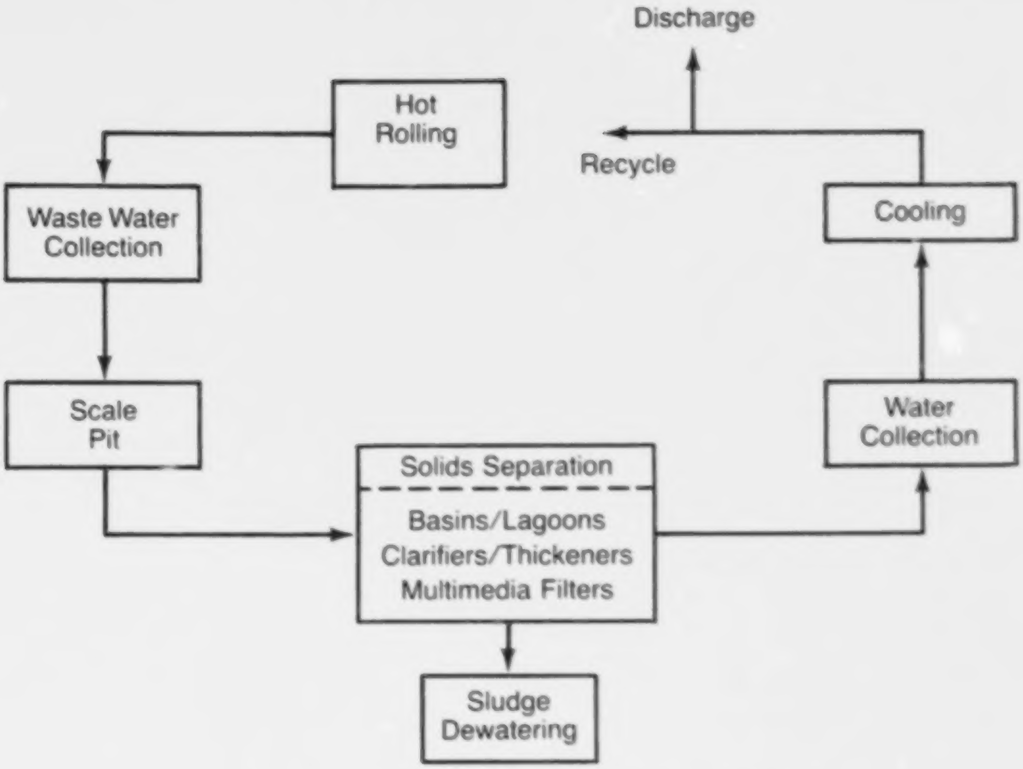
Discharge
Hot Rolling
Recycle
Waste Water Collection
Cooling
Scale Pit
Water Collection
Solids Separation
Basins/Lagoons
Clarifiers/Thickeners
Multimedia Filters
Sludge Dewatering

Figure 1. Typical rolling-mill wastewater treatment system.

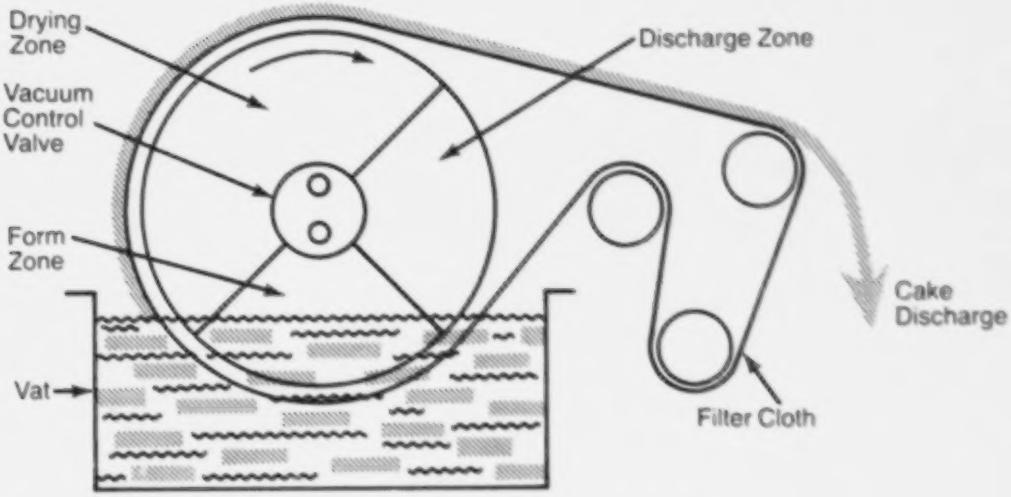
Drying Zone
Discharge Zone
Vacuum Control Valve
Form Zone
Cake Discharge
Vat
Filter Cloth

Figure 2. Schematic of a vacuum filter.

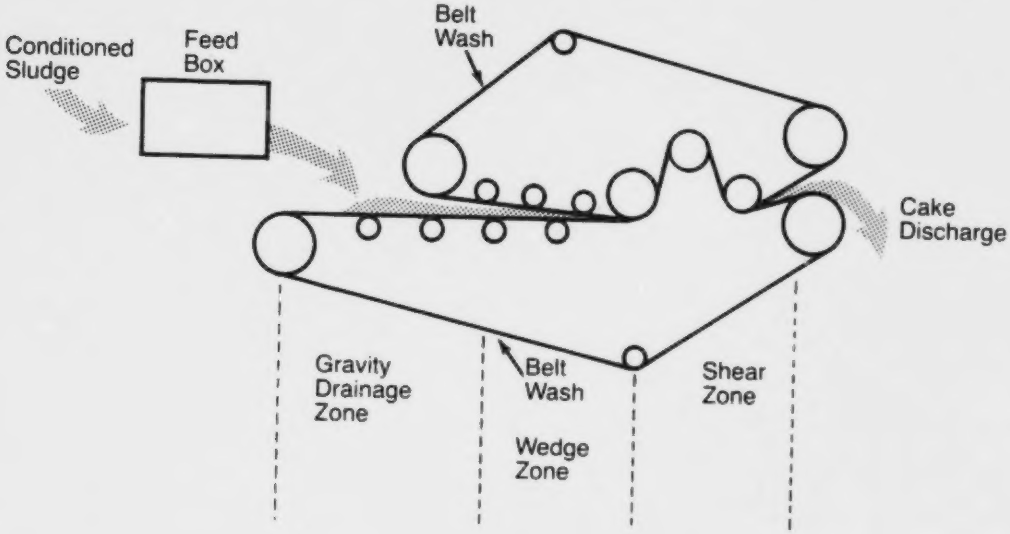
Conditioned Sludge
Feed Box
Belt Wash
Cake Discharge
Gravity Drainage Zone
Belt Wash
Wedge Zone
Shear Zone

Figure 3. Schematic of a belt press filter.

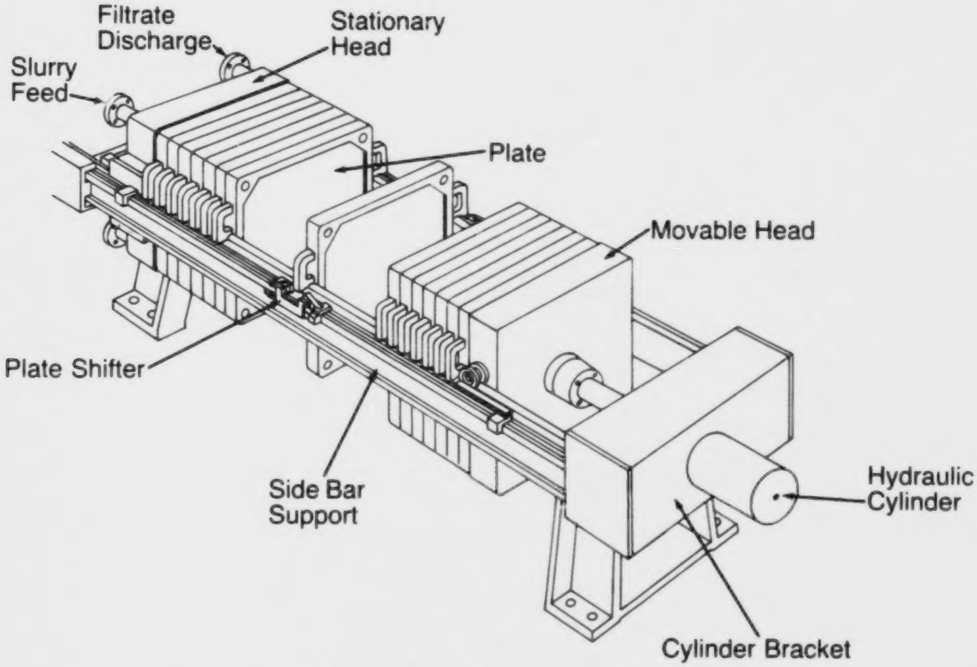
Filtrate Discharge
Stationary Head
Slurry Feed
Plate
Movable Head
Plate Shifter
Side Bar Support
Hydraulic Cylinder
Cylinder Bracket

Figure 4. Schematic of a filter press.

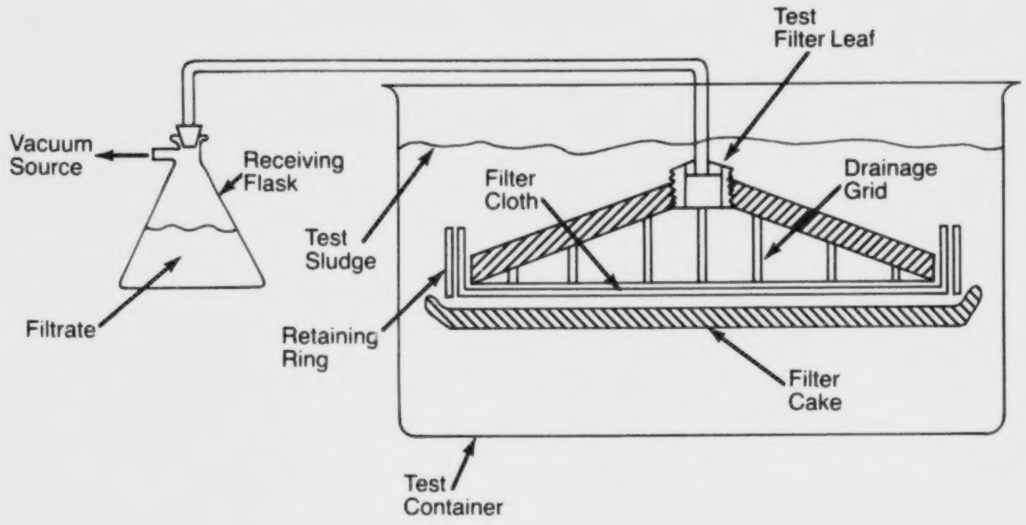
Test
Filter Leaf
Vacuum
Source
Receiving
Flask
Filter
Cloth
Drainage
Grid
Test
Sludge
Filtrate
Retaining
Ring
Filter
Cake
Test
Container

Figure 5. Vacuum filter simulator assembly.

device is capable of producing a vacuum filter cake with characteristics very similar to those from full-scale units and has proven adequate to provide very useful and accurate scale-up parameters. With this type of simple laboratory device in mind, efforts were concentrated on developing such units for belt-press filters and filter presses.

A study was undertaken, utilizing numerous sludge samples from U. S. Steel hot-rolling-mill wastewater treatment systems. As a standard measure of the character of each sludge sample, five properties were determined on each including total solids, total oil, slurry and solids specific gravity, and particle size distribution (by wet screening). A summary of this information is presented in Table 1. It was determined that although various

TABLE 1. TYPICAL CHARACTERISTICS OF ROLLING-MILL SLUDGES

Sludge Source	Total Solids, Percent	Oil,[a] Percent	Oil-to-Solids Ratio	Specific Gravity		Average Particle Size Distribution[b] in Microns, Percent		
				Slurry	Solids	>250	250-44	<44
Hot-Strip Mill	20-50	3-16	1:4.5	1.5	2.3	3	15	82
Primary/Bar Mill	17-54	0.1-1.6	1:50	1.5	4.2	4	35	61
Slab/Plate Mill	26-49	1-9	1:8.5	1.3	2.7	2	8	90
Structural Mill	12-20	3-5	1:5	1.1	2.2	1	23	76

[a] As percent of total solids.
[b] By wet screening.

sludge-generation sources in several plants are similar (such as two hot-strip mills), their respective sludges may have widely varying characteristics. This information was then used to develop relationships between sludge characteristics and dewatering properties.

BELT-PRESS FILTER SIMULATOR DEVELOPMENT

Belt-press manufacturers use simulators of their own design, but no commercial laboratory simulation device has yet been marketed. One of the simplest simulators consists of a plastic/metal screen and a section of hard rubber, whereby wet sludge is manually compressed between the rubber and the screen. This method was evaluated but typical belt-press pressures could not be achieved, filtrate collection was difficult, and reproducible conditions could not be maintained from test to test. At the other end of the spectrum are pilot-size commercially available belt-press filters (up to 0.5-metre belt width, see Figure 3) which can provide thorough dewatering information, but have numerous disadvantages for laboratory testing including size and cost. In between these extremes are batch-test filters employing horizontal-roller devices to press sludge between screens, or static-pressure devices that apply static pressure to the screen-sludge sandwich. After evaluating these alternatives, it was decided to adapt a version of the static-pressure filter for the testing of sludges.

A schematic depicting the final design of the static-pressure belt-press simulator is shown in Figure 6. The gravity-drainage zone of the full-size belt press is simulated by placing the chemically conditioned sludge sample on the lower filter cloth and allowing free water to drain from the device. Early testing had shown that the low-pressure and high-pressure zones of the full-scale unit are best simulated by hydraulically pressing the plates together to apply respective pressures to the sludge of 5 pounds per square inch (psi) for a cycle time of 60 seconds, followed by 40 psi for 30 seconds.

Selection of the optimum belt fabric is important to the success of the belt-press filtration process. The suitability of a fabric for dewatering a particular sludge depends on its material of construction and its weave.2) The composition of a fabric principally determines the releasability of the sludge cake from the belts; fabrics are typically constructed of stainless steel, polypropylene, polyester, etc. The weave of the fabric affects both the formation of the cake and its subsequent release. An open weave may allow extrusion of the solids particles through the mesh openings, while too tight a weave causes blinding by the solids. Belt fabrics must be sufficiently porous to permit passage of filtrate, but sufficiently tight to obtain a high capture of solids. Monofilament (single fiber) fabrics generally have fewer interstices than multifilament (many single fibers twisted together) fabrics wherein solids may become entrapped. Thus, cake release is often facilitated by filtration with a monofilament fabric.

Conditioning of sludges with polymers is a critical step in the belt-press dewatering process.3) Such polymers are usually synthetically produced polyelectrolytes designed to enhance the separation of solids from liquids. A

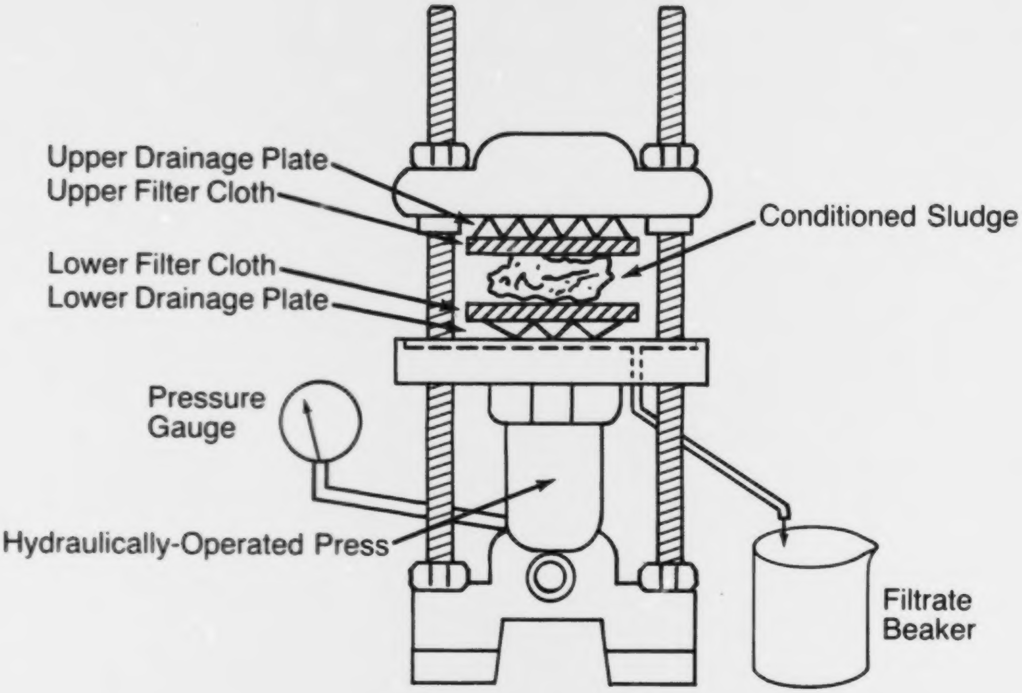
Upper Drainage Plate
Upper Filter Cloth
Conditioned Sludge
Lower Filter Cloth
Lower Drainage Plate
Pressure Gauge
Hydraulically-Operated Press
Filtrate Beaker

Figure 6. Belt press filter simulator assembly.

polymer causes the solid particles to clump together, thereby increasing their effective size. This "superflocculation" achieves the following objectives:

1. Converts capillary water to free water which drains readily in the gravity zone and initial stage of the wedge (low compression) zone; the moisture loading to the belt press is therefore decreased and the solids throughput is increased.

2. Increases the effective diameter of the sludge particles, thereby decreasing the amount of small particles extruding through the belt and improving solids capture.

3. Forms a more rigid cake and allows more pressure to be applied without extrusion, which increases the dryness of the sludge cake.

The ionic character (anionic, cationic, or nonionic), molecular weight, and charge density of a polymer determine how effectively the polymer chains attach themselves to the suspended particles in the sludge. Because each individual sludge visually has a distinct dewatering character, it is difficult without testing to predict the specific polymer that would perform best in each dewatering application. Therefore, polymer screening tests are normally conducted to evaluate a particular sludge sample with a series of polymers of different ionic character, molecular weight, and charge density. Selection of the correct polymer is normally signified by the formation of a mound of agglomerated solids independent from the liquid portion of the sludge. This mass of curdled solids in free water indicates that the sludge has been properly conditioned and is ready for dewatering by belt press.

After the appropriate belt fabric and polymer conditioning has been determined, the belt-press simulation test is performed and information recorded. A 250-millilitre sample of characterized sludge after polymer conditioning is placed between the plates of the laboratory simulator as depicted in Figure 6. Filtrate is channeled through the recess under the lower drainage plate and is collected in a beaker and the volume measured for each of the three operating cycles (gravity drainage, initial compression, and full compression). Cake solids are also noted during each of the three cycles and appearance, release, and extrusion are observed. Finally, an overall filterability rating is assigned based on the recorded information. The ratings are excellent, good, fair, marginal, and failure.

SIMULATOR TESTING

Typical results from laboratory belt-press simulator trials are shown in Table 2. In general, rolling-mill sludges dewatered well in the belt-press simulator. A further breakdown of the test results as compared to physical properties of the sludge is shown in Table 3. From the data in Tables 2 and 3, certain conclusions were evident.

TABLE 2. BELT-PRESS FILTER SIMULATOR TESTING

Sludge Source	Raw Sludge Solids, Percent	Sludge Conditioning		Simulator Filter Cake Solids, Percent			
		Polymer	Water Separation	Gravity Drainage	Low Pressure	High Pressure	Cake[a] Release
Hot-Strip Mill	60	Anionic	None	61	75	82	Good
	46	Anionic	None	47	68	80	Good
Primary/Bar Mill	51	Non-ionic	Good	66	70	75	Excellent
	55	Cationic	Fair	71	81	81	Good
	42	Cationic	Good	75	82	84	Excellent
Slab/Plate Mill	56	Cationic	None	58	74	75	Good
Structural Mill	15	Cationic	Good	63	73	76	Fair

[a] From the simulator belt.

It was observed that the specific gravity of the dry sludge solids correlated with ease of dewatering of hot-rolling-mill sludges. The higher the specific gravity the better the dewatering on the simulator.

Iron content of the sludge solids is another physical characteristic which has a direct relationship with belt-press filterability because of the density of iron oxide. The greater the iron content of the solids in sludges, the greater is the specific gravity of the dry solids.

TABLE 3. PHYSICAL CHARACTERISTICS OF ROLLING-MILL SLUDGES VERSUS FILTERABILITY ON BELT-PRESS SIMULATOR

Sludge Source	Specific Gravity of Dry Solids	Iron Content as Percent of Total Solids	Oil as Percent of Total Solids	Filterability on Simulator[a]
Hot-Strip Mill	2.08	27.4	23.6	Good
	2.64	36.0	23.0	Good
Primary/Bar Mill	4.64	36.7	2.4	Excellent
	4.30	28.8	0.9	Excellent
	3.35	35.4	2.9	Good
Slab/Plate Mill	4.16	30.2	2.2	Excellent
	2.55	26.2	17.9	Good
	2.37	27.3	17.7	Good
Structural Mill	2.21	6.7	34.1	Fair

[a] Filterability is based on overall consideration of sludge conditioning, thickness and appearance of sludge cake, cake release, and cake solids content.

Certain generalizations were also made in relationships between oil and grease content of the sludges and their filterability.

1. All sludges rated excellent in dewatering contained low (0 to 3 percent) oil and grease contents (as percentages of oil to the total solids in the sludges).

2. Sludges with medium (3 to 30 percent) oil and grease contents generally exhibited good filterabilities.

3. As the oil and grease contents increase to 30 percent or higher, belt-press filterability becomes marginal and fair ratings are more likely.

COMPARISONS WITH FULL-SCALE BELT-PRESS FILTERS

Batch dewatering tests of samples of various steel-mill sludges were performed on a small commercially available belt press with the assistance of The Nalco Chemical Company,4) and results compared to tests with the same samples on the belt-press simulator. Cake solids content appeared to be the most logical factor for relating the units and so it was chosen as the basis for comparison.

This comparison was accomplished by regressing the cake solids from the belt press on the cake solids from the simulator. The resulting equation describing this relationship is

$$Y = 2.659 + 1.075X \qquad (1)$$

where y is the percent cake solids content for the belt press and X is the percent cake solids content for the simulator. This simple relationship accounts for 98 percent of the total variability in the belt-press cake solids content for the dewatering test samples used in its derivation. Subsequent use of this equation to predict the cake solids content for rolling-mill sludges has been very satisfactory. The maximum deviation between predicted and observed belt-press cake solids content has been 3 percent. The difference in dewatering efficiency between the simulator and the belt press is attributed to shear forces induced in the sludge by the belt press that cannot be duplicated by the simulator.

FILTER PRESS SIMULATOR DEVELOPMENT

Filter presses, as illustrated in Figure 4, are an alternative to vacuum filters or belt-press filters for dewatering steel-mill sludges. However, their application to steel-mill wastes has been somewhat limited in the past. U. S. Steel utilizes several units in applications that are very specific and limited in scope, and no broad-based study had been done to determine the general applicability of the unit to a wider variety of wastes.

A survey of commercial filter presses and many of their applications revealed that a recessed-cavity chamber filter press, either fixed or variable (diaphragm) volume, would produce a filter cake with potentially the highest possible solids content (compared to vacuum filters and belt presses), and is applicable to the dewatering of most categories of sludges, even those with a high oil content.

The fixed-volume recessed-chamber plate is a modification of the common plate and frame design. The frame has been eliminated and both sides of the filter plate have been modified to a concave design, having about 1/2- to 1-inch-deep depression. This modification reduces the volume per plate but enables the filter cake to drop by gravity from the filter cloth when the press is opened and the plates spread.

The diaphragm press is a further modification of a fixed-volume recessed chamber plate filter press as described above. An elastomeric diaphragm is incorporated into the plate forming one side of the recessed chamber. After this recessed chamber plate has been filled with filter cake, hydraulic (or pneumatic) pressure is applied behind the diaphragm, extending it and compressing the filter cake. Elastomeric diaphragms are used with metal plates but one-piece, molded polypropylene plates with polypropylene membranes (diaphragms) have been available for about 5 years.

A means of simulating both the fixed- and variable-volume units was needed in order to screen sludges potentially applicable to this operation. Recessed chamber plate filter presses with 1-square-foot (or larger) diaphragms are available as pilot units, but these were considered unacceptably large for this investigation because of the large volume of feed samples required. Therefore, a smaller bench-scale press was constructed to meet the requirements of the study.

Functions of a laboratory filter press that would provide meaningful data were: (1) a quick filling, 1-liter volume filter, which would be capable of diaphragm adaptation and of operation up to a pressure of at least 300 pounds per square inch gage; (2) permit measurements of filter cake characteristics; (3) could be operated either as a fixed or a variable-volume unit; (4) provide sufficient filter cake for testing; and (5) could be quickly dismantled for cleaning and rapid reassembly.

A small laboratory simulation pressure filtration unit was designed and assembled as shown in Figure 7. It is a batch-type unit with a working volume of about 950 milliliters (ml) and a filter area of 62.0 square cm (cm^2). An 18-mesh, stainless-steel, wire screen inserted in the shallow recess of the filter base plate supports the filter media. The unit can be readily charged through a Swagelok fitting in the top flange, and compressed-nitrogen gas provides the driving force. To install a diaphragm to simulate a variable-volume unit, the upper cylindrical sections of the filter body can be removed until the remaining sections are at or just above the top of the remaining filter cake. Any thin rubber sheeting with good stretching properties can function as a diaphragm. The rubber diaphragm is placed across the top of the remaining filter-press body section and the unit is reassembled. Nitrogen is again admitted to the desired pressure and maintained until the diaphragm squeeze, or secondary filtration, is completed. After releasing the cake from the section(s), it is weighed and dried to determine the solids content. All

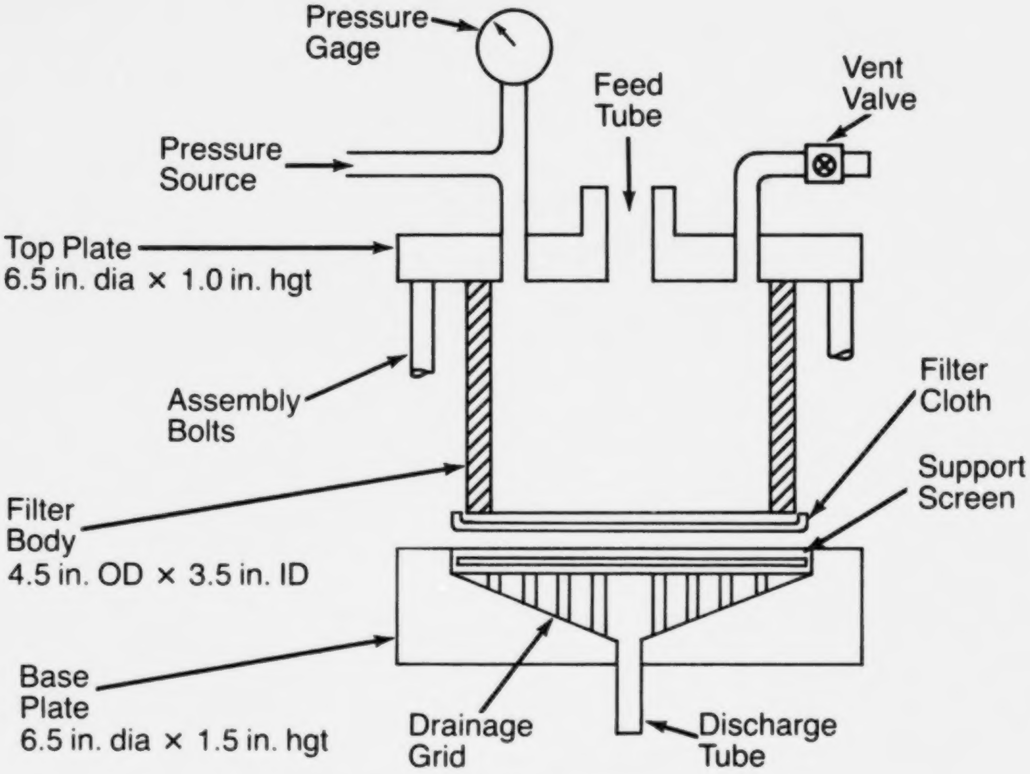
Pressure Gage
Feed Tube
Vent Valve
Pressure Source
Top Plate
6.5 in. dia × 1.0 in. hgt
Assembly Bolts
Filter Cloth
Support Screen
Filter Body
4.5 in. OD × 3.5 in. ID
Base Plate
6.5 in. dia × 1.5 in. hgt
Drainage Grid
Discharge Tube

Figure 7. Filter press simulator assembly.

filtration tests were performed with a polypropylene filter media. Very good release of each formed cake was achieved with this media.

A procedure for operating this simulator device was developed through extensive testing of samples taken from various U. S. Steel rolling mills. This also indicated that sludge with a wide variety of characteristics could be successfully processed through the simulator.

A modification was made to the standard filter-press operation both to minimize excessive premature blow-through of gas and to test for the advisability of utilizing a variable-volume filter. In variable-volume operation, a flexible diaphragm is utilized to squeeze extra water from a filter cake, after the filter chamber has been filled in a fixed-volume mode. This is useful if the filter cake is compressible, where the particles will deform under applied pressure. First, the fixed chamber is pressurized to about 120 psig pressure (primary phase), which is the pressure commonly used in commercial presses. Then the diaphragm is installed and activated to squeeze the cake further (secondary phase). The diaphragm not only prevents a premature blow-through of gas, but also simulates the filled-chamber squeezing of a fixed-volume unit or the diaphragm compression of a variable-volume unit. Therefore, any sludge sample can be tested in a single operation both for filterability and for compressibility. If this secondary squeezing indicates a final volume decrease of less than 25 percent, the sample is considered a candidate for a fixed-volume filter press. If the decrease is more than 50 percent, it is considered a candidate for a variable-volume filter press.

In the simulator press, the primary phase is considered to be completed when the gas used as the driving force has pushed out essentially all the filtrate that can be discharged at this pressure. The gas is immediately shut off so minimal gas is blown through the cake. The diaphragm for the secondary filtration phase is then installed and nitrogen gas is admitted above the diaphragm. An applied constant pressure of 210 psig was used in most of the tests. This secondary filtration is considered complete when the filtrate flow has either "appreciably" decreased or has stopped.

SIMULATOR TESTING

Data from selected filter-press development tests, with hot-rolling-mill sludges, are summarized in Table 4. The secondary filter cakes for all the hot-rolling mills were 80 to 90 percent solids, higher than experienced with other dewatering devices, but in several cases the filtration rates were unacceptably low. Based on the small increase in solids content during secondary filtering, all these cakes were considered noncompressible and should dewater successfully with a fixed-volume filter press, with little advantage to be gained by the use of a variable-volume unit. When a lime admix was used, the rate of increase in solids content was much higher, indicating higher filtration rates, and the cakes approached the compressible state. The addition of lime increased the secondary solids content in sludges from the slab and plate mill and the hot-strip mill, but more importantly provided large increases in the filtration rates, enhancing the projected capacity of a full-scale unit.

TABLE 4. FILTER PRESS SIMULATOR TESTING

Sludge Source	Filtration Aid (Lime), Percent of Dry Solids	Total Solids, percent Raw Sludge	 Primary Filter Cake	 Secondary Filter Cake	Percent Solids Increase Primary to Secondary Filter Cake	Filtration Rate, Pounds dry Solids per Square Foot per Hour Primary Filtration (120 psig)	 Secondary Filtration (210 psig)
Hot-Strip Mill	0	54	85	90	6	1.8	1.3
	10	48	67	89	33	15.0	5.0
Primary/Bar Mill	0	51	83	89	7	13.0	8.0
Slab/Plate Mill	0	42	73	79	8	1.1	0.6
	1	40	68	86	26	11.3	2.4
	5	40	69	86	25	23.0	4.3
	10	40	69	85	26	34.0	6.0
Structural Mill	0	15	70	87	24	2.3	1.3

To indicate the cake dryness that can be achieved, the weight percent solids in the filter cake is plotted against time, as in the examples in Figure 8. This graph depicts both the primary and secondary filtration operations; the times marking the start of the secondary filtration phases are indicated.

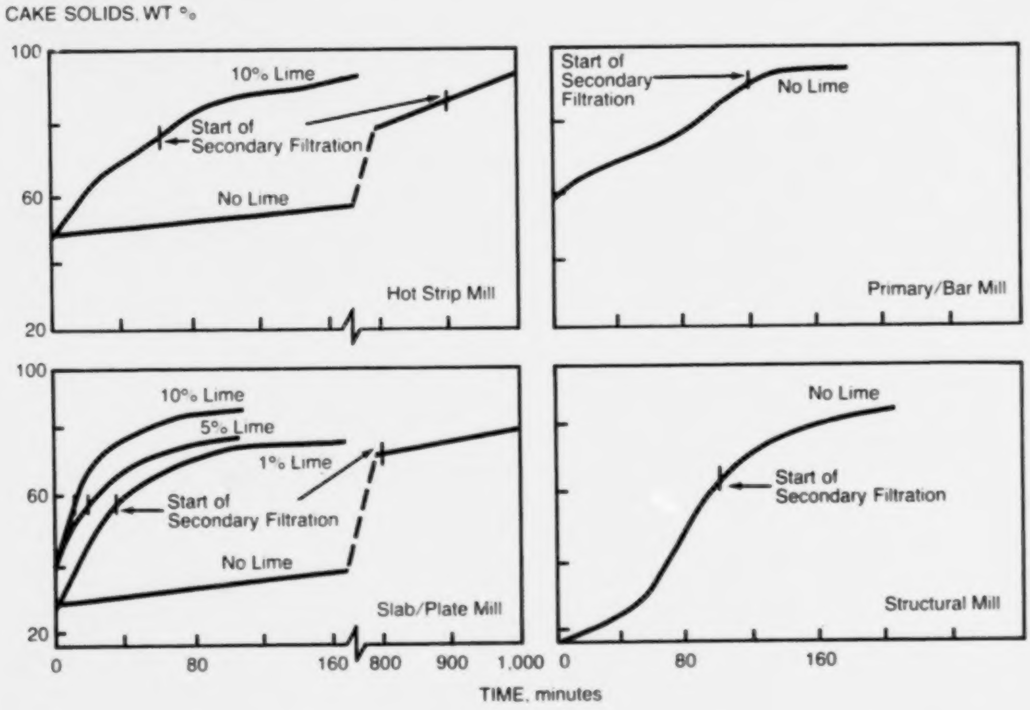

Figure 8. Filter press simulator filtration curves.

The changeover from primary to secondary appears as a smooth transition. Because the filter cake can be viewed as a multiplicity of capillaries, the nitrogen pressure, which is the driving force in the simulator, accelerates removal of the final water that is contained within these capillaries. This surge of filtrate produces an upswing in the curves denoting a rapid increase in solids content in a short time increment at the end of the primary filtration phase. An erroneous extrapolation of this primary filtration phase curve could lead to speculation that the secondary filtration phase is superfluous; this is not the case. The solids content in the primary filter cake at this point is at its maximum for the selected driving pressure. Further dewatering to a higher solids level can be accomplished by a secondary filtration phase with a compressive force (the diaphragm), aided by a higher driving pressure, that will realign the relative position of the cake particles.

Figure 9 depicts the dry-solids production rates as the filtration pressure and the size of the filtration batch are varied in the laboratory filter press. Filter cake thickness was found to be linear with the size of the filter batch. Although higher filtration pressures will produce higher dry-solid production rates, greater increases can be achieved by control of

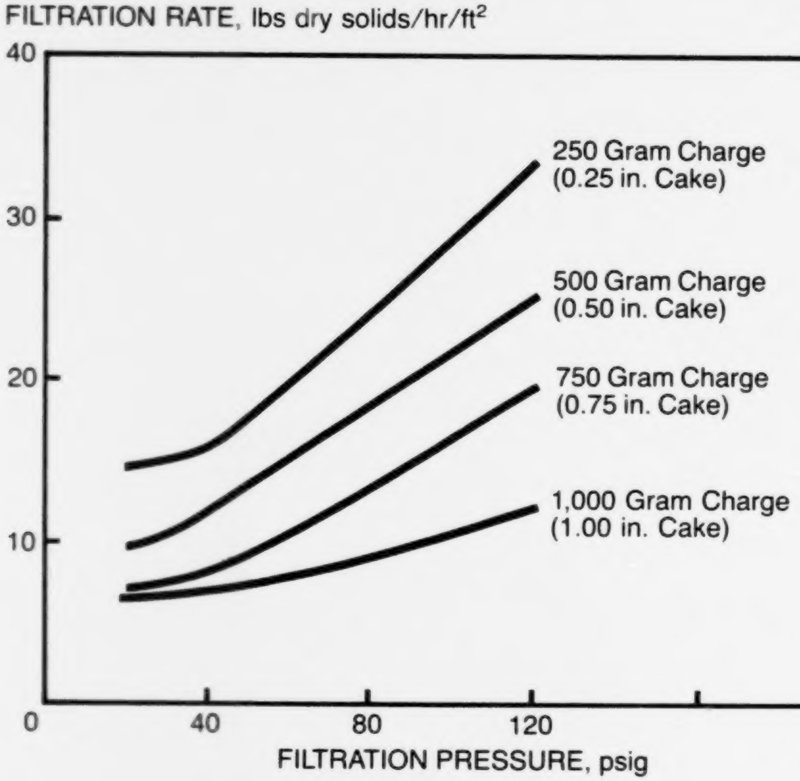

Figure 9. Filter press simulator variable study.

the filter cake thickness and the solids concentration of the feed slurry. Accordingly, dry-solids production rates given in the tables are valid only for the stated experimental conditions and should not be considered absolute values.

COMPARISONS WITH FULL-SCALE FILTER PRESSES

U. S. Steel currently has no full-scale filter presses on rolling-mill applications that could be used as a simulator comparison. Therefore, exact scale-up factors could not be determined for the unit. However, similar devices utilized by equipment manufacturers are often scaled up on a 1:1 basis for both solids content and filtration rate, and it is believed that this would probably also apply to the U. S. Steel simulator.

The unit was compared in the field with presses used in two other applications: (1) an electrogalvanizing zinc sludge, and (2) a boiler-house lime-slurry waste. Simulator results indicated a relationship very close to 1:1 for both solids and rate compared to the full-scale units when the simulator pressure cycle was stopped at the initial sharp decrease in filtration rate. When filtration with the simulator continued until the filtration essentially stopped, the cake solids were generally 10 percent higher and filtration rate 10 percent lower than with the full-scale units.

CONCLUSIONS

Testing has indicated that both the belt-press and the filter-press filtration simulators may be used as basic tools to screen hot-rolling-mill sludges for dewaterability. As in the case of the vacuum filter-leaf device, they can demonstrate the viability of dewatering a particular sludge while also predicting the final cake solids achievable. In addition, tests will indicate where further testing by pilot-scale units is warranted.

Polymer addition was required for successful belt-press simulation and lime addition enhanced filter-press simulator operation. Rigid filter cakes were generated in both units which in many cases would be acceptable for landfilling or reuse.

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4. Information generated in a joint development study of belt-press filtration between U. S. Steel and Nalco Chemical Company.

The work described in this paper was not funded by the U. S. Environmental Protection Agency and therefore the contents do not necessarily reflect the view of the Agency and no official endorsement should be inferred.

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THE HIGH DENSITY SLUDGE PROCESS
AN IMPROVED TECHNOLOGY FOR HYDROXIDE PRECIPITATION OF HEAVY METALS

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ABSTRACT

The High-Density Sludge (HDS) process is an improved cold-lime neutralization technique developed by Bethlehem Steel Corporation and originally applied to produce dense sludges in acidic iron-bearing wastewaters such as coal-mine drainage and pickling rinsewaters from steel plant operations. The results of recent laboratory studies are presented that demonstrate the ability of the HDS process to precipitate efficiently, other heavy metals. In laboratory tests with dilute solutions containing copper, cadmium, nickel, lead, and zinc the HDS process was able to reduce all of the soluble metal concentrations to less than 0.1 ppm at a single pH level. This has not been possible with conventional neutralization. Settled sludge concentrations were greater than 20% solids as compared with a normal 1% solids achieved by conventional neutralization techniques.

INTRODUCTION

In the late 1960's Bethlehem Steel's Research Department developed the High-Density Sludge (HDS) process to treat iron-bearing acid mine drainage (AMD) from its bituminous coal mining operations. The process is shown schematically in Figure 1. The main advantage of the HDS process over conventional cold-lime neutralization of AMD is that it can produce a sludge containing up to 50% solids by weight. By comparison, the conventional process generally produces sludges containing 1 to 2% solids by weight. Thus, there is a very substantial reduction in the volume of sludge generated. The HDS process produces a dense sludge by mixing a controlled amount of previously precipitated solids with the an alkaline agent in a separate reactor and using this mixture to neutralize the acidity and precipitate the soluble metals in the wastewater.

In 1979 and 1980 Bethlehem evaluated the potential for using the HDS process to remove both iron and manganese from an AMD discharge at its anthracite mining operations near Tamaqua, Pennsylvania. The bituminous AMD's which Bethlehem had successfully treated with the HDS process contained high ratios of iron to manganese concentrations, e.g., 150 ppm to 200 ppm of iron and 2 to 3 ppm of manganese. The manganese removal was thus enhanced by co-precipitation of relatively large amounts of iron. The anthracite AMD, however, contained only 30 ppm of iron and 13 ppm of manganese. Thus, the beneficial effects of co-precipitation of iron on manganese removal would be much smaller. As part of this program, a small-scale HDS plant was operated on-site for several months. The results of those on-site tests showed that the HDS process reduced the soluble manganese concentrations to levels much lower than expected. A pH of approximately 9 in the HDS process produced manganese removals equivalent to conventional neutralization at a pH of about 10. The HDS process also produced sludge containing up to 50% solids while conventional neutralization sludge contained about 2-3% solids.

In order to study these observations further, additional laboratory studies were carried out with synthetic solutions containing varying amounts of manganese and iron. The results of those studies, shown in Figure 2, demonstrated that: (1) The HDS process precipitated manganese at a lower solution pH than conventional neutralization; (2) the benefits of the co-precipitation of iron on manganese removal in conventional neutralization were carried through and enhanced by the HDS process; and (3) the HDS process produced dense sludges from all of the solutions tested, including one which contained 50 ppm of manganese but no iron. Because of the success seen in these manganese precipitation studies, the test program was expanded to compare the conventional neutralization process and the HDS process for the precipitation of other heavy metals, including the effects of co-precipitation of iron on both processes.

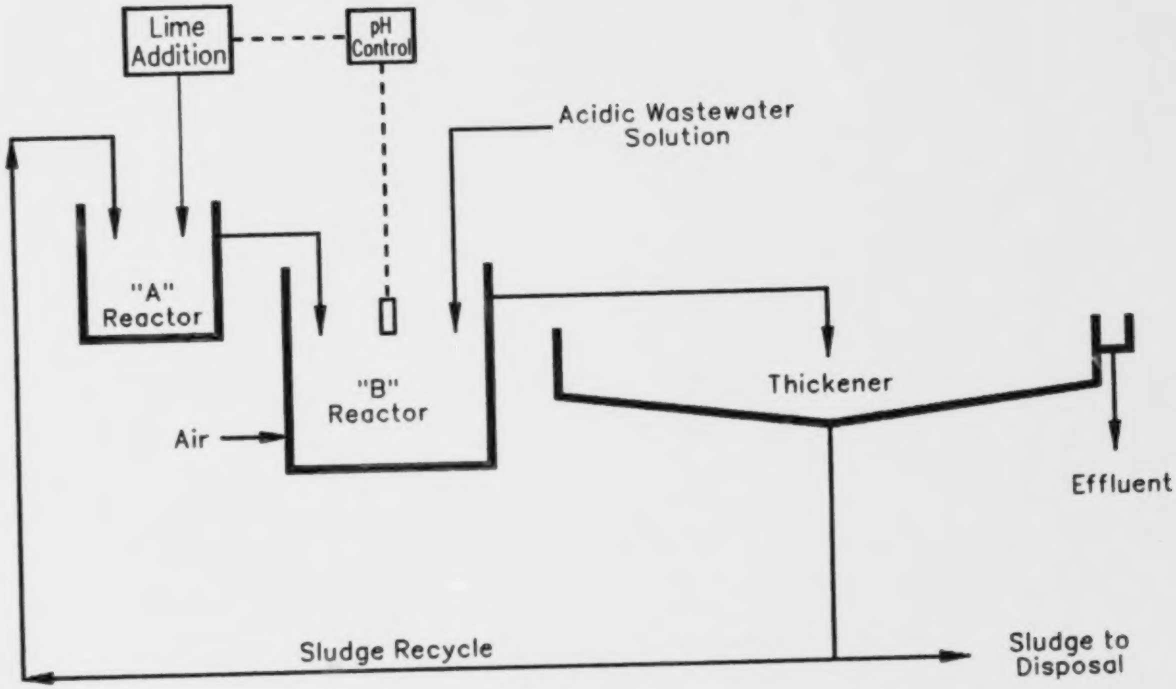
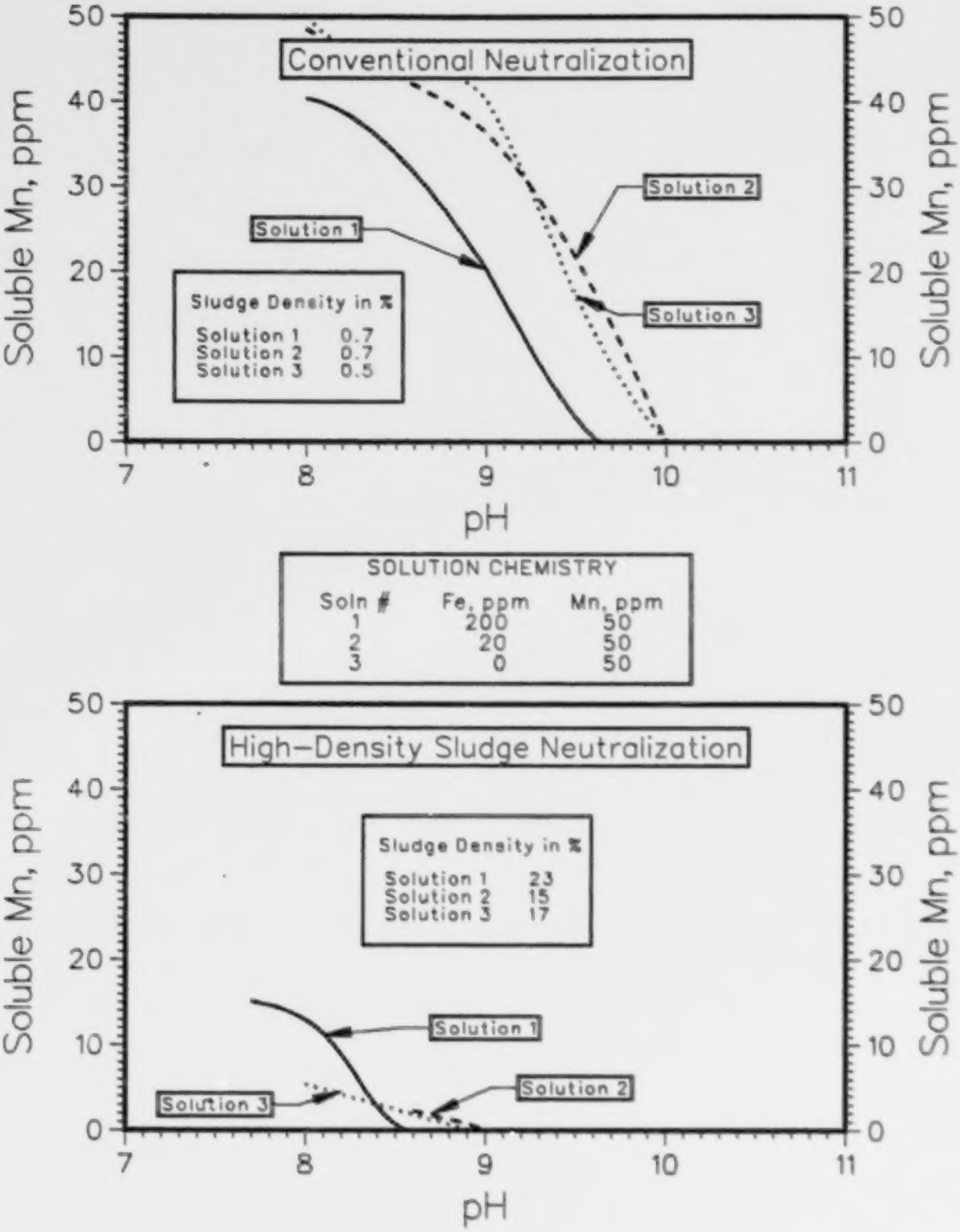

Lime Addition
pH Control
Acidic Wastewater Solution
"A" Reactor
"B" Reactor
Air
Thickener
Effluent
Sludge Recycle
Sludge to Disposal

Figure 1. Schematic Diagram of the High Density Sludge Process



SOLUTION CHEMISTRY

Soln #	Fe, ppm	Mn, ppm
1	200	50
2	20	50
3	0	50

Figure 2. Comparison of Conventional Neutralization and the High–Density Sludge Process for the Precipitation of Manganese

TEST PROGRAM

Sets of soluble, heavy metal concentrations versus pH were generated for both conventional and HDS neutralization of synthetic solutions containing cadmium, nickel, zinc, copper, and lead. The initial metal concentrations of the seven solutions tested are given in Table 1. The free acidity of all solutions was maintained at 245 ppm, which was sufficient to assure complete solubilization of the metal chloride salts. The effects of co-precipitation of iron were determined by varying the amount of soluble iron in the synthetic wastewaters. All metal analyses were performed by flame and carbon furnace atomic absorption spectrophotometry. It must be emphasized that this study deals only with soluble metal concentrations, not total metal concentrations upon which effluent discharge limitations are based.

CONVENTIONAL NEUTRALIZATION

Test Procedure

The variables in the experiments were the iron to total non-ferrous heavy metal ratio, the concentration of non-ferrous heavy metals, and the pH of the neutralized solution. Conventional neutralization tests were conducted by neutralizing a 25 or 35-liter sample of the synthetic solution with lime slurry. All solutions were aerated during neutralization, and samples were taken at pH 8.0, 8.5, and then every 0.25 pH unit until pH 11.25. After standing for about three hours, the neutralized samples were filtered and the filtrates analyzed for heavy metals. The lime demand and the solids formed upon neutralization were also determined at each pH level. The percent solids at final dilution (concentration of solids after the slurry had settled for 24 hours) were determined at pH 10 for all solutions. Three replicate neutralizations were run for each of the solutions. Figures 3 and 4 and the top plots in Figures 5 through 9 present the results of the conventional neutralization tests. The concentration of soluble iron in the neutralized samples never exceeded the minimum detectable limit of 0.01 ppm and thus is not shown in any of the plots.

Tests with No Iron in Solution

The top plots in Figures 8 and 9 represent the results of neutralizations of solutions containing 50 ppm each and 5 ppm each of the non-ferrous heavy metals but no iron. In all cases the metal concentrations in these two figures are lower than those predicted from

TABLE 1. SOLUTION CHEMISTRIES TESTED AND SLUDGE CONCENTRATIONS PRODUCED BY CONVENTIONAL NEUTRALIZATION AND THE HIGH-DENSITY SLUDGE PROCESS

Solution #	Metals Concentration, ppm						Percent Solids in the Settled Sludge			
							Conventional Neutralization		HDS Neutralization	
	Fe	Cd	Ni	Zn	Cu	Pb	% Solids	pH	% Solids	pH
1	250	50	50	50	50	50	0.8	10.0	30	9.5
2	25	50	50	50	50	50	0.8	10.0	23	9.5
3	250	5	5	5	5	5	0.6	10.0	20	8.5
4	25	5	5	5	5	5	0.6	10.0	Not Tested	
5	138	28	28	28	28	28	1.0	10.0	Not Tested	
6	0	50	50	50	50	50	0.9	10.0	25	10.2
7	0	5	5	5	5	5	1.0	10.0	28*	9.0

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* Iron sludge generated separately was used as the recycle slurry.

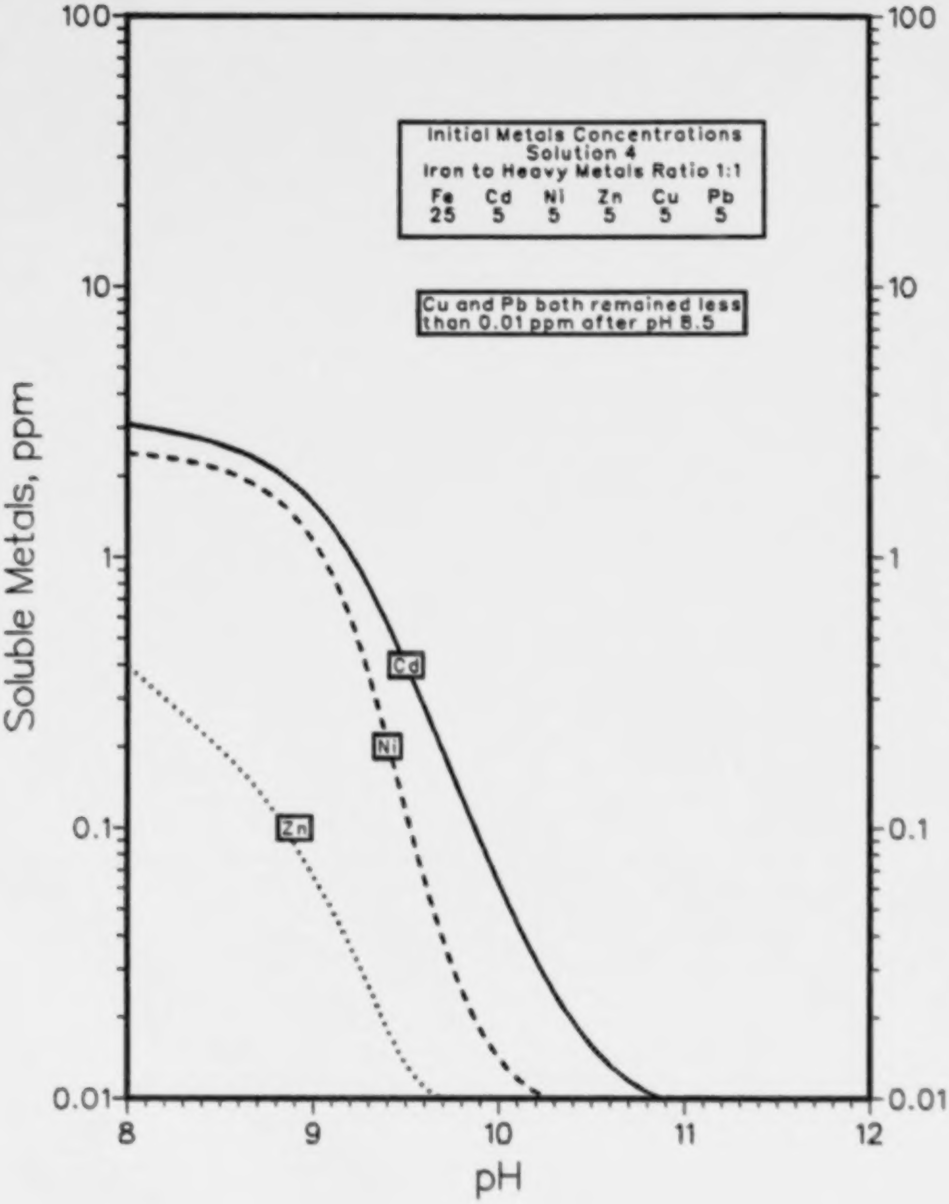

Figure 3. Conventional Neutralization of Solution 4

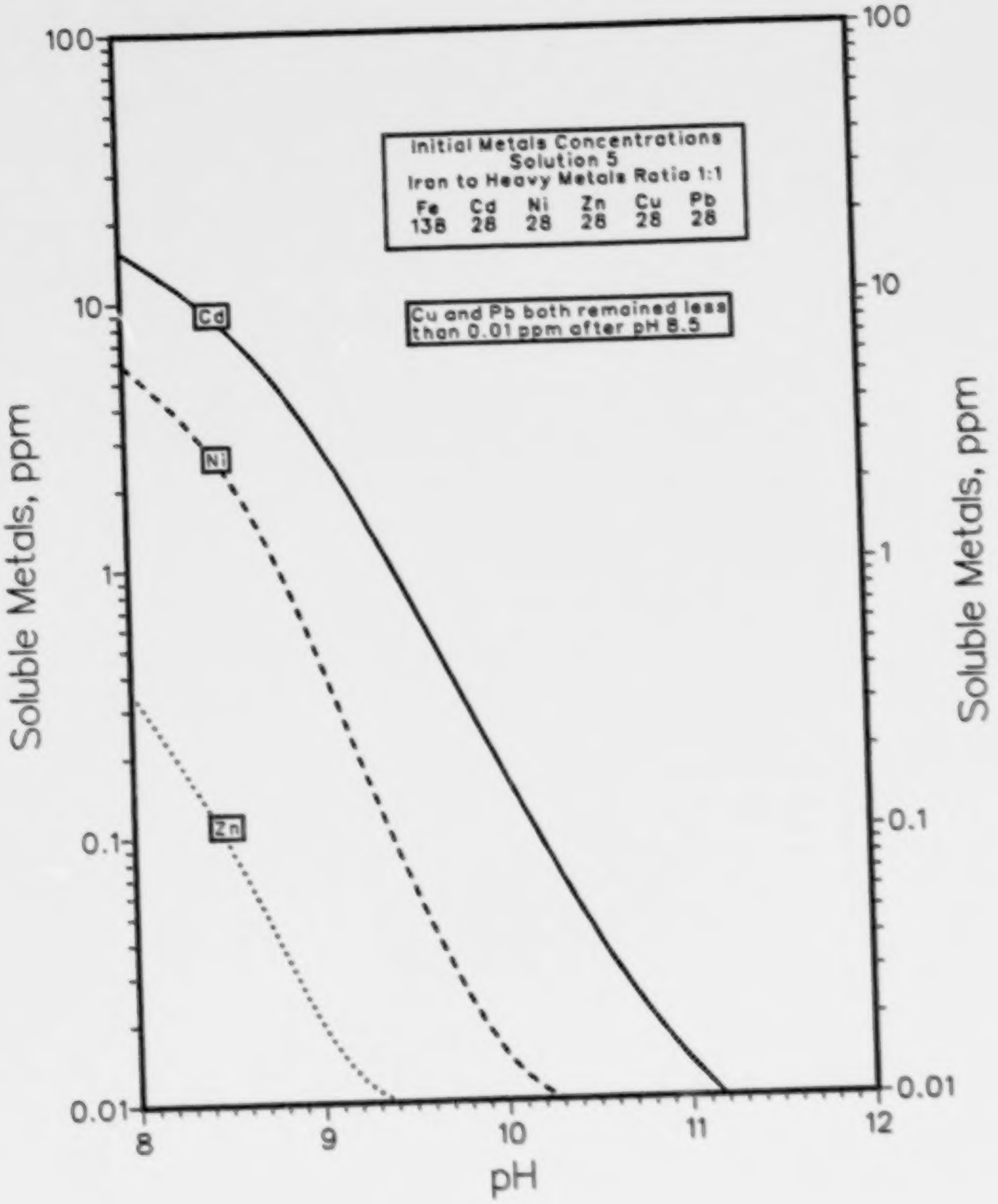

Figure 4. Conventional Neutralization of Solution 5

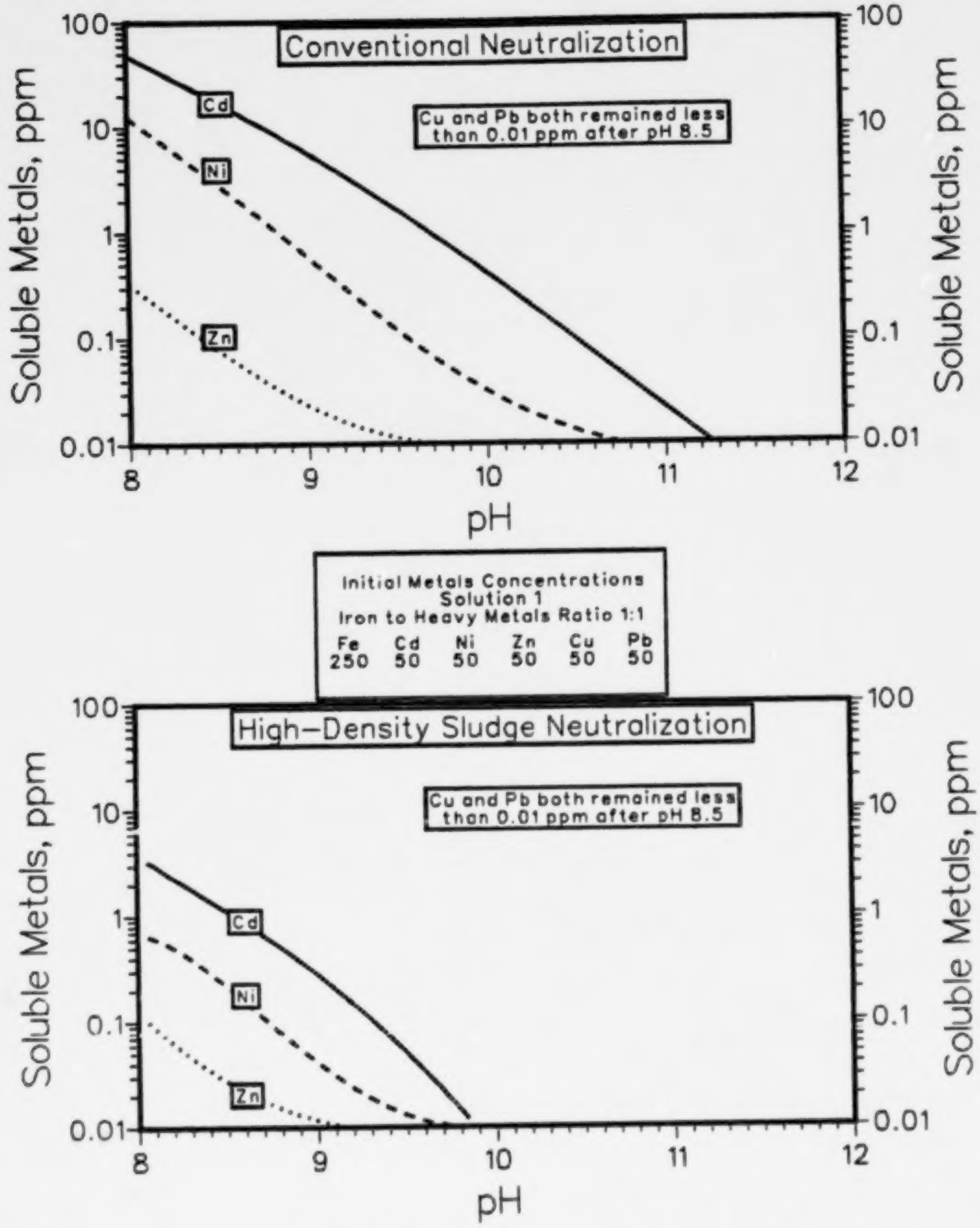

Figure 5. Comparison of Conventional and High–Density Sludge Neutralization of Solution 1

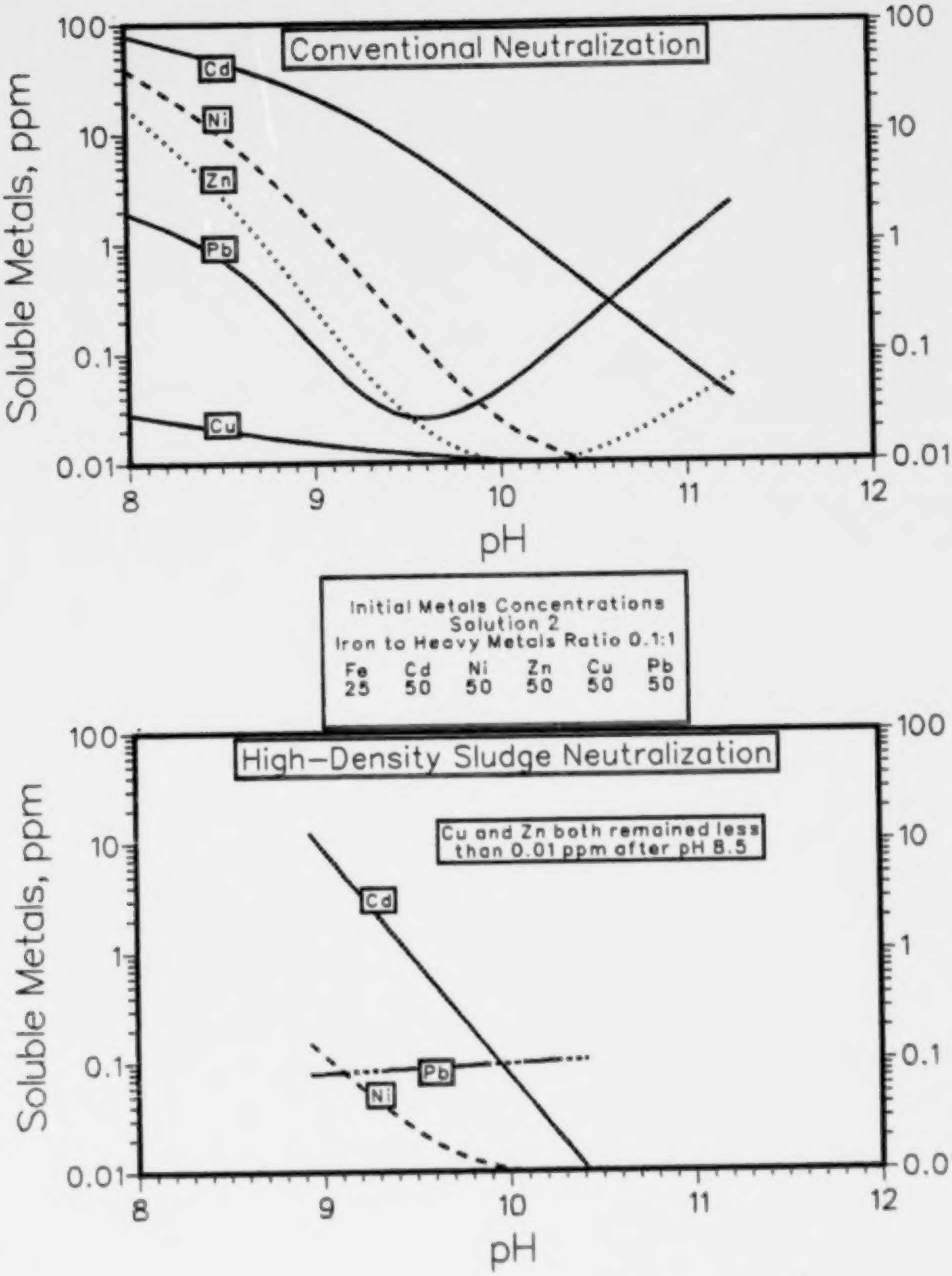

Figure 6. Comparison of Conventional and High–Density Sludge Neutralization of Solution 2

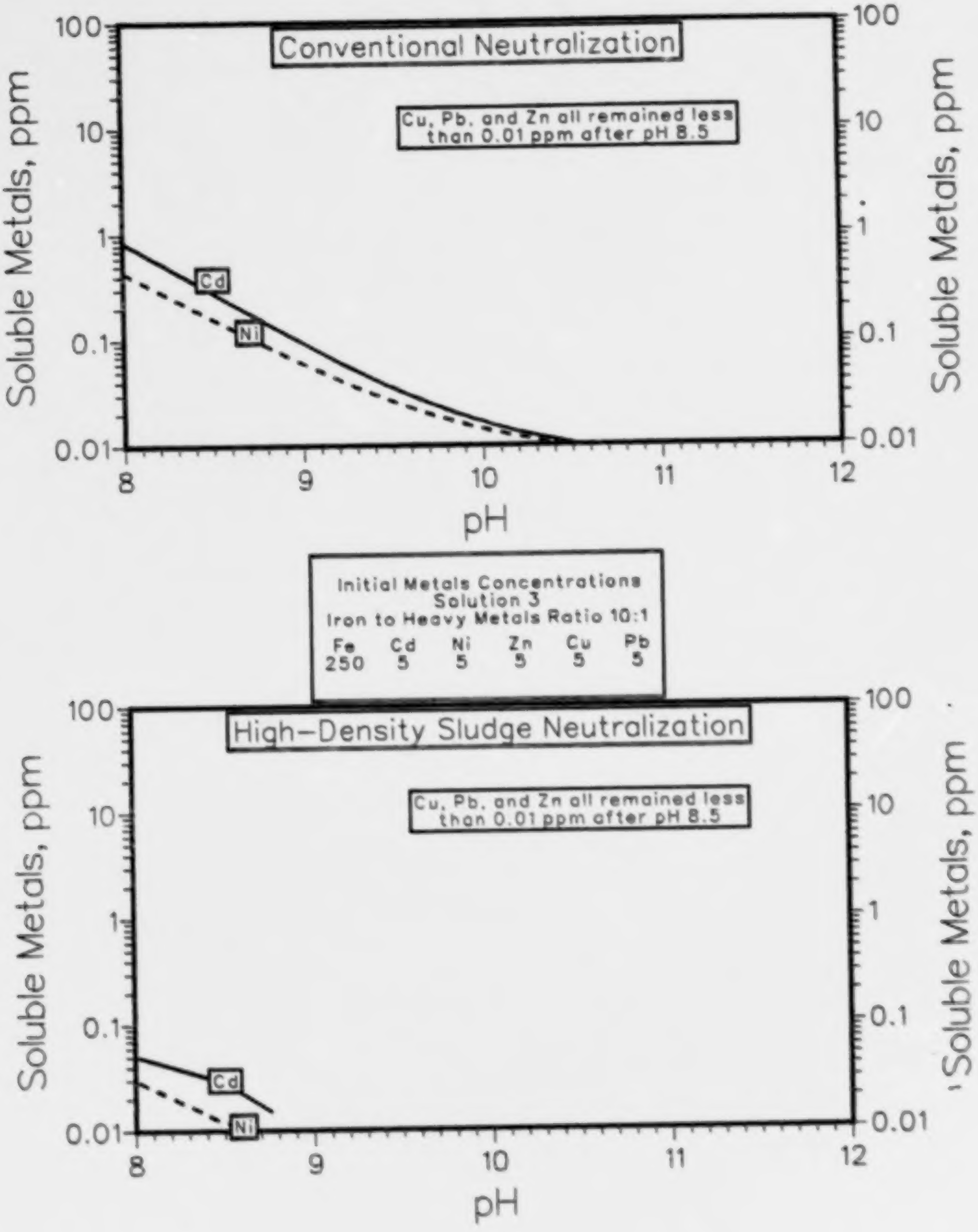

Figure 7. Comparison of Conventional and High-Density Sludge Neutralization of Solution 3

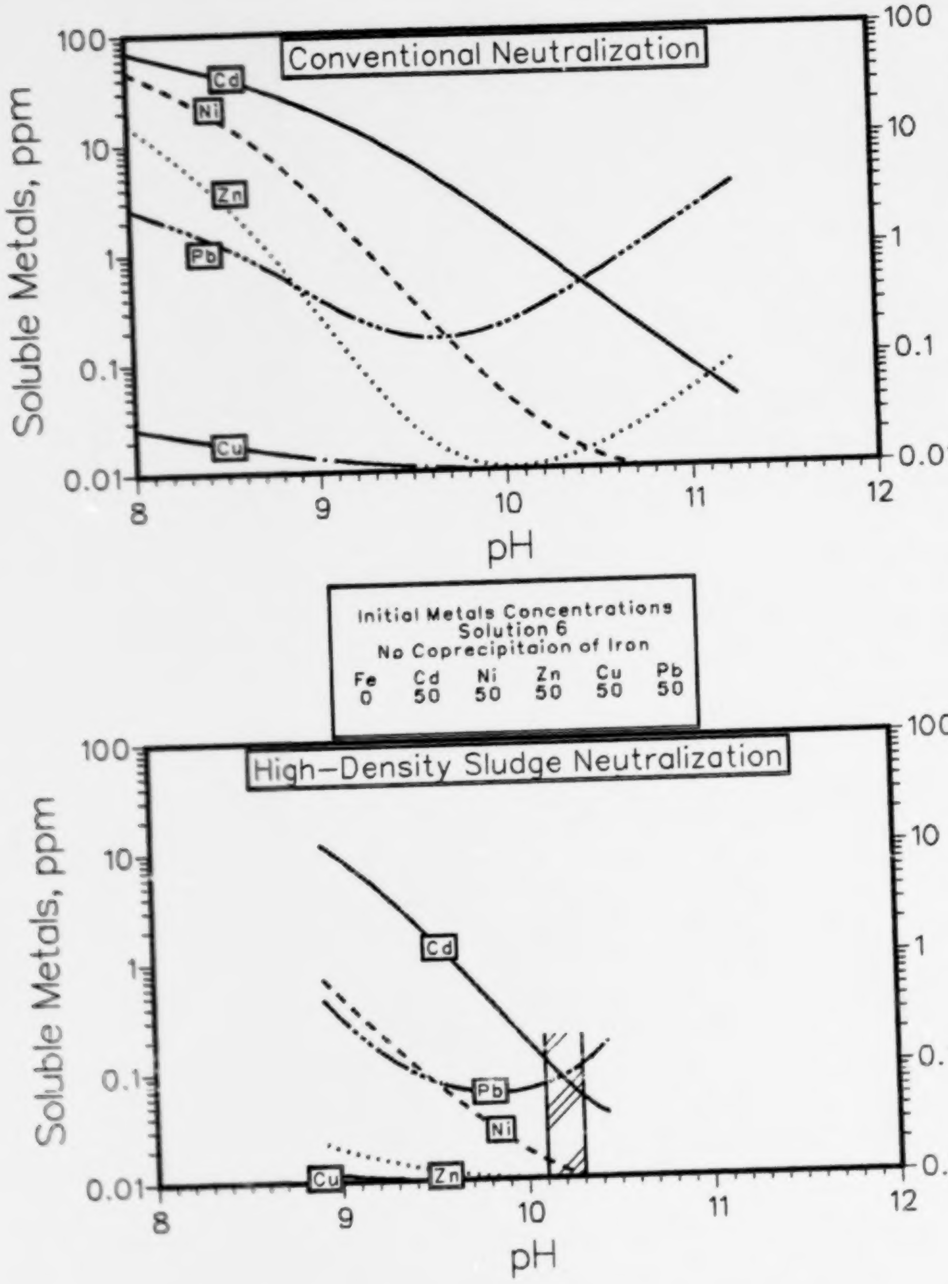

Figure 8. Comparison of Conventional and High–Density Sludge Neutralization of Solution 6

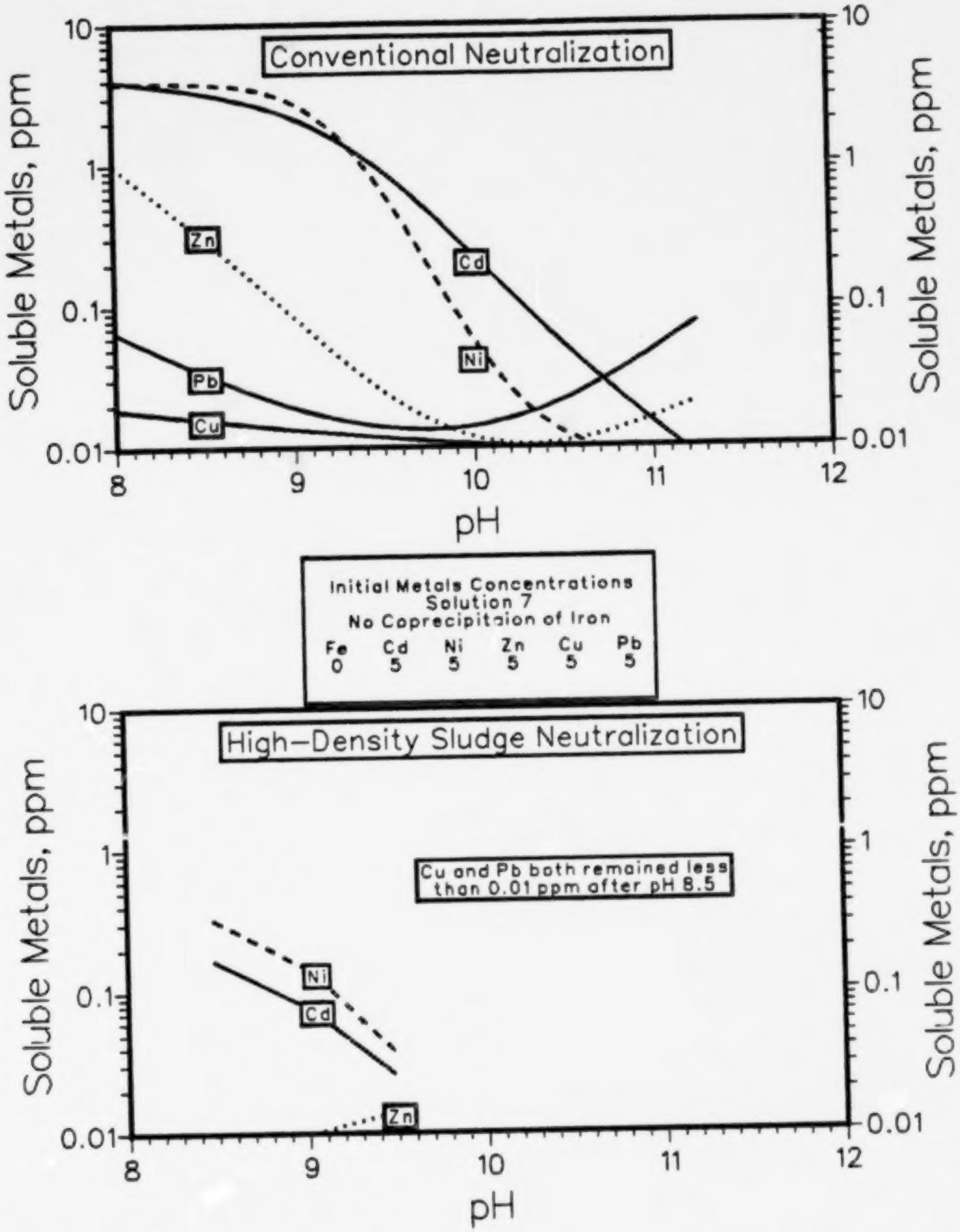

Figure 9. Comparison of Conventional and High–Density Sludge Neutralization of Solution 7

solubility data. This is probably due to co-precipitation effects of one metal on another, e.g., the precipitation of copper affects the precipitation of nickel and so on. For the purposes of this test program, the data in the top plots in Figures 8 and 9 were considered the base cases for determining the effects of co-precipitation of iron, and also the effects of the HDS process, on the solubilities of the non-ferrous heavy metals.

Effects of Iron on Metals Precipitation

As expected, the data show that the co-precipitation of iron both reduces the pH necessary to precipitate the non-ferrous heavy metals and reduces the minimum solubilities attainable by hydroxide precipitation. At the higher iron concentrations tested, the amphoteric properties of lead and zinc were eliminated, i.e., the metal hydroxides did not resolubilize as the pH was increased. The data further show that the effects of co-precipitation are more pronounced as the ratio of iron to non-ferrous heavy metals is increased. For example, comparison of the top plots in Figures 5 and 6 show the results of conventional neutralization of two solutions which both contained 50 ppm each of cadmium, nickel, zinc, copper, and lead. The solution in Figure 5 also contained 250 ppm of ferrous iron (iron to total non-ferrous metals ratio of 1:1) while the solution in Figure 6 contained only 25 ppm of ferrous iron (iron to total non-ferrous metals ratio of 0.1:1). Comparison of these plots shows that the higher iron to non-ferrous heavy metals ratio reduced the pH necessary to precipitate the non-ferrous metals and also eliminated the amphoteric properties of the zinc and lead. Similar results can be seen when comparing Figure 3 (iron to total non-ferrous heavy metals ratio of 1:1) with the top portion of Figure 7 (iron to total non-ferrous heavy metals ratio of 10:1). The data also show that, for a given iron to total non-ferrous heavy metals ratio, the beneficial effects of co-precipitation, especially for cadmium and nickel, are more pronounced for lower initial non-ferrous heavy metals concentrations. This can be seen by comparing Figures 3, 4, and the top plot in Figure 5. All of these solutions have an iron to total non-ferrous heavy metal ratio of 1:1. However, as the initial cadmium and nickel concentrations increase, the pH required for their precipitation increases.

Sludge Density

One of the major drawbacks to the use of conventional lime neutralization is the generation of a difficult-to-dewater sludge which contains very low solids concentrations. Table 1 lists the final dilution solids concentrations obtained in the conventional neutralization tests. Although the addition of ferrous iron aided in the removal of the non-ferrous heavy metals, it also greatly increased the volume of sludge generated. For example, the addition of 250 ppm of iron to a solution containing 50 ppm each of cadmium, nickel, zinc, copper, and lead doubled the solids formed upon neutralization.

HIGH-DENSITY SLUDGE NEUTRALIZATION

Test Procedure

All HDS tests were performed in a laboratory-scale unit which was operated 24 hours per day, five days per week at an acid flow rate of approximately 145 ml/min. The process was considered to be in equilibrium when the solids concentration of the recycled sludge reached 10%. Each pH test point in the HDS program was maintained for a minimum of one week. Daily samples of the raw acid solution and thickener effluent were taken for soluble heavy metals analysis. The solids concentration in the thickener underflow and the lime demand were also determined daily. Due to time constraints, only five of the synthetic solutions tested in the conventional neutralization study were tested in the HDS system.

Test Results

The results of the HDS neutralization studies are presented in the bottom plots in Figures 5 through 9. The concentration of soluble iron in the thickener effluent never exceeded the minimum detectable limit of 0.01 ppm and thus is not shown in any of the plots. Several conclusions can be drawn by comparing the HDS neutralization curves with those for conventional neutralization of the same solutions.

- At any given pH, the HDS process produced lower soluble cadmium and nickel concentrations than conventional neutralization.

- For the amphoteric metal hydroxides (zinc and lead), the HDS process produced minimum solubilities at approximately the same pH level as conventional neutralization. However, even without the benefit of the co-precipitation of iron, the HDS process reduced the amount of lead and zinc which resolubilized when pH levels were increased above the minimum solubility point.

- There was only one case, lead in solution 2 (Figure 6), in which the HDS process failed to produce minimum soluble metal concentrations as low or lower than those achieved by conventional neutralization.

- For those solutions which contained no iron, the HDS process was able to reduce all the soluble heavy metal concentrations to less than 0.1 ppm in the pH range 10.1 to 10.3. Conventional neutralization techniques were unable to reduce the soluble metal concentrations of all of the metals to less than 0.1 ppm.

HDS Treatment With Separately Generated Iron Sludge

The HDS testing of solution 7, which contained 5 ppm of each of the non-ferrous heavy metals but no iron, was conducted in a different manner from the other HDS tests. Since solution 7 generated very few solids upon neutralization, it would have taken an extremely long time to generate enough sludge to recycle. A dense sludge was generated by using the HDS process to neutralize a solution containing 500 ppm of ferrous iron. This sludge was then used as the recycle slurry to test the removal of non-ferrous heavy metals from solution 2. The results of this test are shown in the bottom plot of Figure 9. This was the only test in which cadmium was removed at a lower pH than nickel. Also, while the average metal concentrations were reduced to low levels at relatively low pH values, the individual daily analytical results were the most widely scattered of all the tests. Although time constraints did not permit additional experimentation, this variation of the HDS process could be very useful for treating solutions containing low initial concentrations of soluble heavy metals.

Sludge Density

The HDS process produced dense sludges for all five solutions tested. Table 1 lists the sludge densities produced from each solution by conventional and HDS neutralization. It is obvious that the HDS process greatly reduces sludge disposal problems, especially if co-precipitation of iron is utilized to obtain minimum heavy metal concentrations. For example, conventional neutralization of 500 gpm of solution 1 would produce about 55 gallons per minute of sludge containing 0.8 % solids. The HDS process would produce 1.2 gpm of sludge containing 30 % solids by weight.

Lime Requirements

Although the HDS process removes metals at a lower pH value than conventional neutralization, the lime demands for both processes are the same for identical metals removal efficiencies.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ALKALINE AND BREAKPOINT CHLORINATION FOR THE CONTROL OF CYANIDE AND AMMONIA IN STEEL INDUSTRY WASTEWATERS

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ABSTRACT

This study is concerned with an assessment of the physical/chemical treatment technology to achieve the BAT effluent limitations when applied to the wastewaters from the by-product cokemaking and blast furnace processes. The emphasis is on the use of chlorination processes as part of a physical/chemical methodology to control cyanides and ammonia in ironmaking wastewaters. A review of the chlorination reactions with cyanides and ammonia, as well as organic compounds, was carried out. These reactions can result in the formation of undesirable products such as halomethanes, chloramines, chlorophenols, and other chloroorganics.

Pilot plant investigations, as well as full scale plant data, were examined to determine the effectiveness of the technology to reliably achieve the effluent limitations for both types of wastewaters. Although free cyanides are destroyed, the stable complex iron cyanides are not; thus, compliance with a total cyanide limitation will depend on the concentrations of these refractory substances present in the original wastewaters. Some other problems associated with the chlorination processes are discussed.

Cost estimates reported for full scale plants based on pilot plant data were reviewed and critiqued. These estimates are generally low when compared to operating plants and the industry's experience.

INTRODUCTION

This study is concerned with achieving the BAT limitations by physical/chemical methods. More specifically, it treats solely with the use of aggressive chlorine oxidation of the pollutants cyanide, ammonia, and phenols; the removal of metals is not considered. The emphasis will be on the pollutants found in ironmaking wastewaters, which are also found in by-product coke wastewaters in much higher concentrations. The treatment method is essentially the same, but the treatment cost is much higher for by-product coke wastewaters.

The chlorination process can be considered as consisting of two stages; alkaline chlorination carried out at a pH of 10 or higher where cyanide is readily oxidized to cyanate, and breakpoint chlorination accomplished at a pH of 7.0 to 8.5 where cyanate, ammonia, and phenols are destroyed. Care must be taken in the alkaline chlorination stage to maintain the pH at 10 to prevent the evolution of the toxic gas, cyanogen chloride. Electrodes which measure oxidation-reduction potential (ORP) can be used to monitor and control chlorine feed and a pH electrode controller-feeder is used to maintain the proper alkalinity. At breakpoint, the second oxidation step, the cyanate is oxidized to N_2 and CO_2, ammonia is oxidized to N_2 and water, and phenol to CO_2 and water. Care must be taken to add sufficient chlorine to prevent the formation of chlorophenols.

To minimize the potential toxicity of excess chlorine concentrations in treated ironmaking wastewaters, dechlorination using reducing agents such as sulfur dioxide or sulfites, are added in sufficient quantities to react with excess residual chlorine, forming nontoxic chlorides.

The Final Development Document for Effluent Limitations, Guidelines, and Standards for the Iron and Steel Manufacturing(1) lists six BAT treatment alternatives. Of these, the EPA has selected BAT alternate 4. Recirculation of treated wastewaters with minimum blowdown is one of the major components of both the BPT and BAT model treatment systems. The blowdown rate was decreased from 125 gal/ton at BPT to 70 gal/ton at BAT. The BAT-4 limits are based on the alkaline chlorination of this blowdown. The treatment includes the two-stage chlorination process previously mentioned.

CHEMISTRY OF CHLORINATION

The following discussion presents a description of some of the chemical reactions involved in the chlorination of cyanide, ammonia, and phenol.

When chlorine gas is dissolved in water, a reverse hydrolysis occurs as follows:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

However, when the acid chlorine solution is applied to a wastewater and the pH after chlorination is above pH 7.0, as in the case of the alkaline chlorination of cyanide in wastewater ($pH \geq 10$), the free molecular chlorine is almost instantaneously hydrolyzed to hypochlorous acid, which can then dissociate to the hypochlorite ion (OCl^-) as shown by the equation:

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

The dissociation constant, K_d(2) for this equilibrium is:

$$K_d = \frac{[H^+]\,[OCl^-]}{[HOCl]} = 3.3 \times 10^{-8} \text{ (at 20°C)} \qquad (3)$$

The results of the application of the dissociation constant to various pH values are presented in Figure 1. The percentages of undissociated HOCl and dissociated OCl^- ion (as alkali hypochlorite) are shown at various pH values. For example, at pH 7.5, 50 percent HOCl is present and at pH 10 the chlorine is substantially present as the dissociated OCl^- ion. Thus, the hypochlorite ion predominates in the alkaline chlorination of cyanide in wastewaters as follows:

$$HOCl + NaOH \rightleftharpoons Na^+ + OCl^- + H_2O \qquad (4)$$

At a pH below 7.0 the chlorine is present as hypochlorous acid (HOCl).

The OCl^- ion is the active group for the oxidation of cyanide:

$$OCl^- + CN^- + H_2O \rightleftharpoons CNCl + 2OH^- \qquad (5)$$

The two electrons are provided by the cyanide ion. This reaction takes place at pH 8.5 or above, usually at pH 10.0 where about 99 percent of the chlorine is present as the OCl^- ion. This is referred to as alkaline chlorination. Also, it is the first stage of a two-stage chlorination treatment process.

At lower pH values, about pH 7.0 to 8.5, the hypochlorous acid (HOCl) is the active group for the oxidation of cyanate, ammonia, and phenol. This is what is known as breakpoint chlorination. The oxidation of free cyanide in wastewater with chlorine is a widely practiced process. Chamberlin et al have studied these reactions and have shown them to be stoichiometric, and to progress in two stages. The reactions involved are summarized as follows:

$$\begin{array}{lll}
Cl_2 + 2NaOH & = NaOCl + NaCl + H_2O & (A) \\
NaOCl + NaCN + H_2O & = CNCl + 2NaOH & (B) \\
CNCl + 2NaOH & = NaCNO + NaCl + H_2O & (C) \\
\hline
Cl_2 + NaCN + 2NaOH & = NaCNO + 2NaCl + H_2O & (6)
\end{array}$$

$$\begin{array}{lll}
3Cl_2 + 6NaOH & = 3NaOCl + 3NaCl + 3H_2O & (A) \\
3NaOCl + 2NaCNO + H_2O & = 2NaHCO_3 + N_2 + 3NaCl & (B) \\
\hline
3Cl_2 + 2NaCNO + 6NaOH & = 2NaHCO_3 + N_2 + 6NaCl + 2H_2O & (7)
\end{array}$$

The reaction indicated by equation (6) represents the partial oxidation of cyanide to cyanate. Recognition should be given to the formation of the toxic volatile cyanogen chloride as an intermediate reaction product:

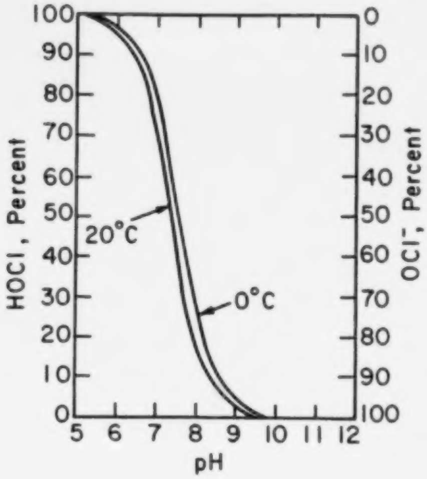
$$OCl^- + CN^- + H_2O \longrightarrow CNCl + 2OH^- \qquad (6B)$$

It is important that the reaction be conducted at pH $\geq$ 10 for the hydrolysis to proceed rapidly:

$$CNCl + 2OH^- \longrightarrow CNO^- + H_2O \qquad (6C)$$

FIGURE 1

RELATIVE AMOUNTS OF HOCl AND OCl⁻ AT VARIOUS pH LEVELS (3)



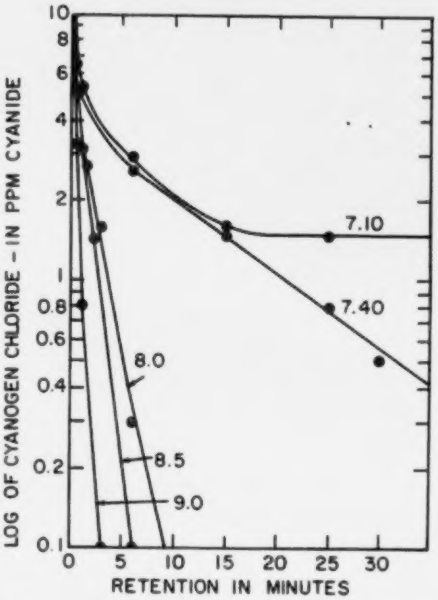
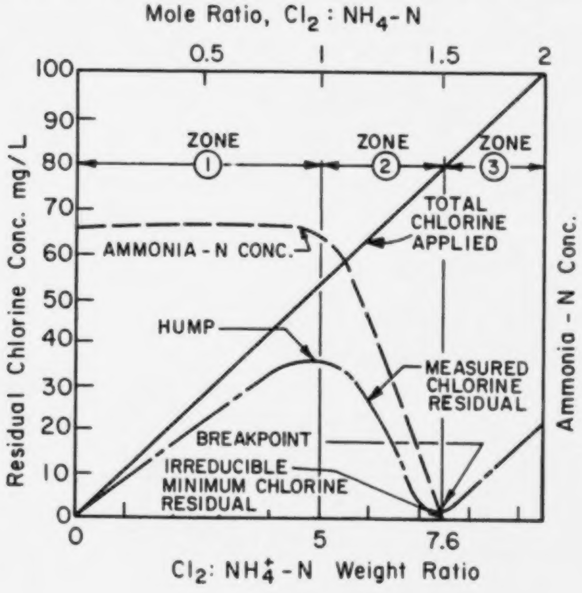


FIGURE 2 EFFECT OF pH ON HYDROLYSIS OF CYANOGEN CHLORIDE TO CYANATES. (2)

FIGURE 3

THEORETICAL BREAKPOINT CHLORINATION CURVE (3)



Chamberlin and Snyder(2) cite the actual oxidation of cyanide (CN^-) to form CNCl (6B) to be instantaneous, while the hydrolysis to CNO^- is primarily pH dependent. Also, the rate of reaction increases with increasing temperatures and with excess hypochlorite. A decrease in cyanogen chloride from 10.0 to 0.1 ppm was reported to occur in three minutes at pH 10, in nine minutes at pH 8, and to be incomplete at pH 7.1 and below. These reaction rates are shown in Figure 2. Thus, high pH values are necessary to prevent the evolution of toxic cyanogen chloride gas.

Equation (7) represents the complete oxidation of cyanate to nitrogen gas and other end products. This second stage utilizes the chlorine in the form of hypochlorous acid (HOCl). Experimental data indicates that destruction of the cyanate would be complete in about five minutes at pH 7.3 - 7.5, while it would take about eighty minutes at pH 9.9.

In the design of an alkaline chlorination process for the destruction of cyanides, process conditions, especially pH, must be controlled to accommodate (a) the hydrolysis of cyanogen chloride which is most rapid at high pH levels (pH 10), and (b) the hydrolysis of cyanate and subsequent oxidation of ammonia which is most rapid at lower pH levels (pH 7).

The theoretical chemical requirements on a weight basis for the oxidation of cyanide to nitrogen and carbon dioxide are; 6.73 parts chlorine per part cyanide, and 1.13 parts caustic soda per part chlorine. In practice, complete oxidation normally requires a minimum dosage of at least 7.4:1, $Cl_2:CN^-$.

While the amenable cyanides (CN_A) are essentially 100 percent converted to cyanate by alkaline chlorination at pH > 10, the strong complex cyanides resist breakdown by hypochlorite. Although ferrocyanide ($[Fe\ (CN)_6]^{4-}$) is oxidized to ferricyanide ($[Fe\ (CN)_6]^{3-}$), further attack by hypochlorite does not occur.

In reference to the capability of alkaline chlorination to destroy cyanides in blast furnace wastewaters, Caruso and Wong-Chong(4) determined from plant surveys that the effectiveness of alkaline chlorination is limited to the oxidation of the free (amenable) cyanides (CN_A). They reported that at one plant the alkaline chlorination process removed about 87.5 percent of the total cyanide (CN_T). At another plant, 86 percent of the total cyanides were amenable to chlorination. Essentially 100 percent of the amenable cyanides were removed, but the complex iron cyanides were not destroyed.

In addition to gaseous chlorine, sodium and calcium hypochlorites have been commonly employed as oxidants for cyanides. Also, the alkali employed for control of pH levels may be lime or sodium carbonate instead of sodium hydroxide.

Removal of ammonia and phenol from blast furnace wastewater can be accomplished by breakpoint chlorination. Breakpoint chlorination (or superchlorination) occurs when sufficient chlorine has been added to a wastewater to cause the chemical oxidation of ammonium in solution to nitrogen gas (N_2) and other end products. If insufficient chlorine is present to achieve breakpoint, chloramines are formed.

Reactions between chlorine and ammonia in dilute aqueous solution can proceed according to a number of competing pathways. Formation of chloramines, termed "combined residual", and nitrate can occur in the following manner:

$$NH_4^+ + HOCl \longrightarrow NH_2Cl \text{ (monochloramine)} + H_2O + H^+ \qquad pH \geq 8.5 \qquad (8)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 \text{ (dichloramine)} + H_2O \qquad pH\ 5 \text{ to } 8.5 \qquad (9)$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 \text{ (nitrogen trichloride)} + H_2O \qquad pH \leq 4.4 \qquad (10)$$

$$NH_4^+ + 4HOCl \longrightarrow HNO_3 + 5H^+ + 4Cl^- + H_2O \qquad (11)$$

The reactions are dependent upon certain process variables, including pH, temperature, contact time, and the initial chlorine to ammonia nitrogen ratio ($Cl_2:NH_4^+ - N$).(5)

Breakpoint chlorination occurs when sufficient chlorine has been added to the wastewater to cause the chemical oxidation of the ammonium ion in solution to nitrogen gas and other end products. The overall reaction may be expressed as follows:

$$NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+ \qquad (8)$$

$$\underline{NH_2Cl + 0.5HOCl \longrightarrow 0.5N_2 + 0.5H_2O + 1.5H^+ + 1.5Cl^-} \qquad (12)$$

$$NH_4^+ + 1.5HOCl \longrightarrow 0.5N_2 + 1.5H_2O + 2.5H^+ + 1.5Cl \qquad pH\ 7.0 \text{ to } 8.5 \qquad (13)$$

Stoichiometrically, the breakpoint reaction of Equation (13) requires a weight ratio of chlorine to ammonia nitrogen of 7.63:1. In plant practice, the actual weight ratio of chlorine to ammonia nitrogen has ranged from about 8:1 to 10:1 due to process variables. Theoretically, four moles of hydrogen ions are generated for every mole of ammonia nitrogen which is oxidized with chlorine gas. The acidity generated at breakpoint must be neutralized, usually by use of either 1.50 parts of sodium hydroxide (NaOH) per part chlorine or 1.05 parts lime (CaO) for each part chlorine. In practice, the alkalinity of the process influent may supply a portion of the total buffering capacity under breakpoint conditions. The chemicals added at breakpoint add greatly to the total dissolved solids (TDS) and result in a substantial operating expense.

The breakpoint chlorination curve is a graphic representation of the chemical relationships which exist as varying amounts of chlorine are added to dilute solutions of ammonia-nitrogen.(6) The point of maximum reduction of chlorine residual is termed "breakpoint". The theoretical breakpoint curve shown in Figure 3 has several characteristic features. The characteristics of the breakpoint curve shown in Zone 1 include principally the reaction between chlorine and ammonia to form the monochloramine. The "hump" occurs at a chlorine to ammonia-nitrogen weight ratio of 5:1 (molar ratio of 1:1). The chemical equilibria of Zone 2 favors the formation of the dichloramine, Equation (9), and at breakpoint the oxidation of ammonia to nitrogen gas, Equation (13). These reactions proceed in competition until, theoretically, a $Cl_2:NH_4^+$ ratio of 7.63:1 is reached. At breakpoint, the ammonium concentration is minimized. To the right of breakpoint, Zone 3 includes the build-up of free chlorine residual, as well as the presence of small quantities of dichloramine, nitrogen trichloride, and nitrate.

The theoretical chemistry must be combined with application fundamentals if proper process designs and operations are to be achieved in full scale wastewater treatment practice. Generally, the presence of high concentrations of ammonia nitrogen and other chemical constituents in wastewater effluents contribute to the discrepancy between some data available from laboratory testing and that collected in actual wastewater treatment applications. The total amount of chlorine which must be added to a wastewater to achieve breakpoint is affected by the chemical nature of the wastewater. Pressley(7) and other researchers have reported that if a continuously functioning breakpoint chlorination process is to be a consistent and reliable environmental engineering unit process, the system must be capable of responding rapidly to changes in ammonia nitrogen concentration, chlorine demand, pH, alkalinity, and flow. Accurate pH control of the process promoted efficient utilization of chlorine while reducing undesirable end products. Also, effective control over breakpoint chlorination requires utilization of accurate and reliable sensory equipment. In this regard, two components deserve special attention; namely, the ammonia nitrogen and free chlorine monitoring elements.

According to reaction rates established by Morris,(3) the reaction between ammonium and hypochlorous acid, Equation (8), to form monochloramine is 99 percent complete in 0.2 seconds at pH 7 and a molar ratio $Cl_2:NH_4^+$ -N of 0.2:1. The optimum reaction pH was shown to be pH 8.3, allowing 99 percent conversion to monochloramine in 0.069 seconds. Obviously, the rate of this reaction is important in breakpoint since it is the first of several sequential reactions. Laboratory studies have shown the breakpoint reaction rate to vary, depending upon pH. At pH levels between 6 and 7, the breakpoint reaction was found to proceed to completion in less than 15 seconds. When reaction rates at pH levels outside the optimum range of pH 6 to 7 were tested, the rate was found to be slowed considerably. At pH 3.5, for example, the breakpoint chlorination reactions were not complete following two hours of contact.

The pH adjustment chemical should be added to the chlorine prior to application of the chlorine solution to the breakpoint chlorination process influent. Without premixing of chemicals, disproportionate mixing of chlorine solution and pH adjustment chemical in the breakpoint reaction zone can result in pockets of liquid not at the desired pH level.

Dechlorination is a unit process which eliminates the active chlorine residual in solution prior to effluent discharge or additional treatment steps. Current emphasis on elimination of chlorine residual from wastewater treatment effluents has resulted in dechlorination requirements in many cases. For ironmaking BAT alternative 4, dechlorination is required as a companion process to breakpoint chlorination. One of the reducing agents used is sulphur dioxide, which is a colorless, pungent gas that hydrolyzes in aqueous solution to form sulfurous acid, a strong reducing agent. When added to a sample containing active chlorine residual (oxidizing agent), the chlorine residual is converted to a non-toxic form, normally chloride ion.

Sulfur dioxide reacts with both free and combined forms of chlorine residual according to the expressions noted below:

$$SO_2 + HOCl + H_2O \longrightarrow Cl^- + SO_4^= + 3H^+ \qquad (14)$$

$$SO_2 + NH_2Cl + 2H_2O \longrightarrow Cl^- + SO_4^= + NH_4^+ + 2H^+ \qquad (15)$$

Both combined and free chlorine residuals are reduced to chloride ion following the reactions. The sulfite ion is correspondingly oxidized to the sulfate ion. Both chloride and sulfate ions are usually present in abundance in wastewater so that the additional increment added by dechlorination is usually insignificant. The predictions of sulphur dioxide dosages required for dechlorination suggest an $SO_2:Cl_2$ molar ratio of 1:1. This corresponds to a weight ratio of 0.9 to 1.0. The rate of reaction between SO_2 in solution and chlorine residual is practically instantaneous.

Chemical oxidation is effective for removal of phenolics from wastewater. A mechanism for oxidation of phenol with chlorine has been presented by Ingols and Ridenour(8) and a substantial research contribution on oxidation of phenolics in cokemaking wastewaters has been reported by Cleary and Kinney.(9) The report gives performance data for oxidation by chlorine, chlorine dioxide, and ozone. From an economic standpoint, chlorine has the advantage of lower cost per unit of oxidizing equivalence as compared to other oxidants, but it is often more tempermental in application and occasionally less effective. Oxidation of phenols with chlorine in the presence of ammonia is ineffective until sufficient chlorine has been added to destroy the ammonia. With some other oxidants, the oxidation of phenolics precedes the destruction of ammonia. Chlorophenols are formed when insufficient chlorine is added to achieve complete oxidation,(10) which requires a pH of 7 to 10. The chlorophenols impart taste and odor to water in concentrations as low as 0.1 mg/L. Low pH promotes formation of chlorophenolic derivatives and at high pH this reaction can be sluggish. On a weight basis, the Cl_2:Phenol ratio required for complete oxidation is 10:1.

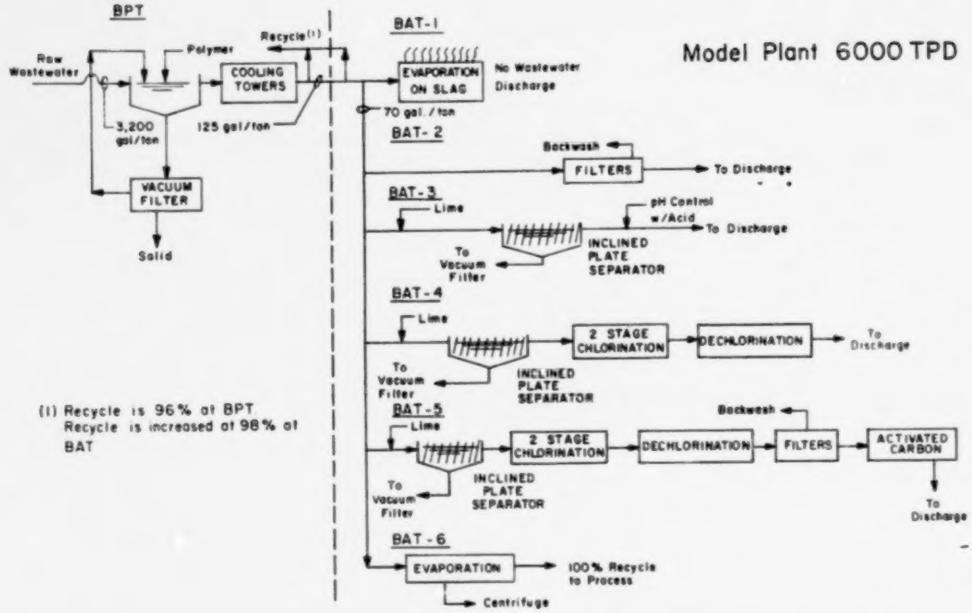
IRONMAKING

Blast furnace wastewaters result primarily from furnace top gas cleaning and cooling. There are six BAT alternatives for the treatment of this wastewater as described in the final development document for effluent limitations guidelines (ELG)(1) Figure 4. The BAT effluent limitations for each alternative are listed in Table 1. The treatment scheme selected by the EPA is BAT alternative 4.

Recirculation of treated wastewater is one of the major components of the BAT treatment system. The blowdown rate of 125 gal/ton at the BPT level was decreased to 70 gal/ton to achieve BAT-4, Figure 5.

The initial step in the treatment of blast furnace wastewater is the removal of suspended solids. Lime (CaO) is added to the blowdown to obtain a pH $\geq$ 10. A thickner or an inclined plate separator is used to remove the suspended solids. Some of the toxic metals and other pollutants which may be entrained in the suspended solids are also removed.

Table 2 lists the model flow, effluent quality, limits, and standards for the selected BAT alternative 4, as well as the BAT feed from BPT treatment. The treatment scheme for BAT-4 includes a two-stage alkaline chlorination process, Figure 5. After the addition of lime to pH 10.5 and subsequent removal of suspended solids, chlorine is added to the alkaline wastewater in the first reactor (first stage) to convert cyanide to cyanate (alkaline chlorination).


Model Plant 6000 TPD

(1) Recycle is 96% at BPT
Recycle is increased at 98% at BAT

BPT
Raw Wastewater
Polymer
Recycle(1)
COOLING TOWERS
3,200 gal/ton
125 gal/ton
VACUUM FILTER
Solid
BAT-1
EVAPORATION ON SLAG
No Wastewater Discharge
70 gal./ton
BAT-2
Backwash
FILTERS
To Discharge
BAT-3
Lime
pH Control w/Acid
To Discharge
INCLINED PLATE SEPARATOR
To Vacuum Filter
BAT-4
Lime
2 STAGE CHLORINATION
DECHLORINATION
To Discharge
INCLINED PLATE SEPARATOR
To Vacuum Filter
BAT-5
Lime
2 STAGE CHLORINATION
DECHLORINATION
Backwash
FILTERS
ACTIVATED CARBON
To Discharge
INCLINED PLATE SEPARATOR
To Vacuum Filter
BAT-6
EVAPORATION
100% Recycle to Process
Centrifuge

FIGURE 4 IRONMAKING ALTERNATIVE TREATMENT MODEL (1)

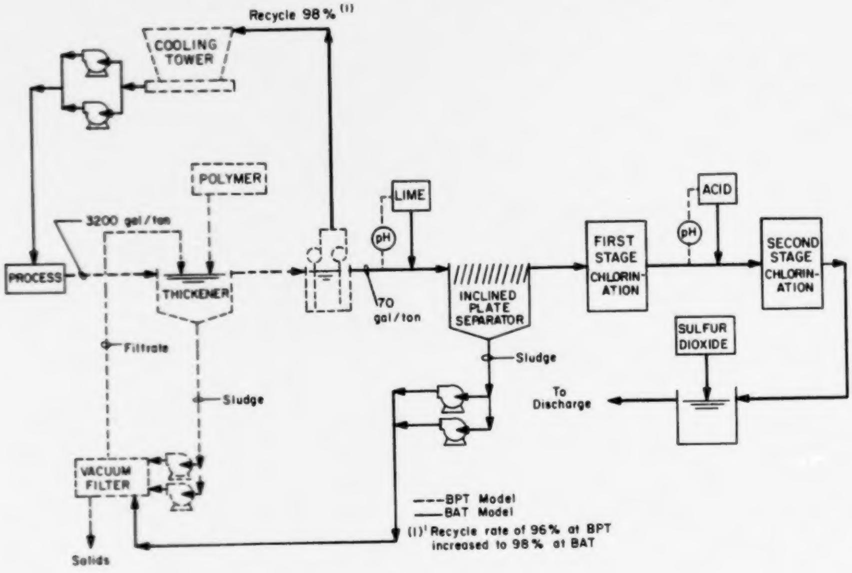
TABLE 1. ALTERNATIVE BAT EFFLUENT LIMITATIONS, IRONMAKING SUBCATEGORY(1)

	BAT-2		BAT-3		BAT-4		BAT-5	
	kg/kkg*	mg/l	kg/kkg*	mg/l	kg/kkg*	mg/l	kg/kkg*	mg/l
Ammonia (as N)								
Average	0.0301	103	0.0301	103	0.002921	10	0.002921	10
Maximum	0.0902	309	0.0902	309	0.008762	30	0.008762	30
Cyanide (T)								
Average	0.00146	5	0.00146	5	0.000292	1	0.000292	1
Maximum	0.00292	10	0.00292	10	0.000584	2	0.000584	2
Phenols (4AAP)								
Average	0.00117	4	0.00117	4	0.0000292	0.1	0.0000292	0.1
Maximum	0.00234	8	0.00234	8	0.0000584	0.2	0.0000584	0.2
Residual Chlorine**								
Maximum	-	-	-	-	0.000146	0.5	0.000146	0.5
Lead								
Average	0.0000730	0.25	0.0000730	0.25	0.0000730	0.25	0.0000730	0.25
Maximum	0.000219	0.75	0.000219	0.75	0.000219	0.75	0.000219	0.75
Zinc								
Average	0.0000876	0.3	0.0000876	0.3	0.0000876	0.3	0.0000876	0.3
Maximum	0.000263	0.9	0.000263	0.9	0.000263	0.9	0.000263	0.9
Flow								
l/kkg		292		292		292		292
gal/ton		70		70		70		70

NOTE 1: Alternatives Nos. 1 & 6, no discharge of process wastewater
NOTE 2: BAT effluent limitations are based upon BAT Alternative No. 4, the selected alternative
* kg/kkg (lb/1000 lb) of product
**The limitation for residual chlorine is applicable only when chlorination of ironmaking wastewaters is practiced

FIGURE 5

IRONMAKING BAT ALTERNATIVE 4 TWO-STAGE ALKALINE CHLORINATION PROCESS (1)


Recycle 98% (1)
COOLING TOWER
POLYMER
LIME
pH
ACID
pH
3200 gal/ton
PROCESS
THICKENER
70 gal/ton
INCLINED PLATE SEPARATOR
FIRST STAGE CHLORINATION
SECOND STAGE CHLORINATION
SULFUR DIOXIDE
Filtrate
Sludge
Sludge
To Discharge
VACUUM FILTER
Solids
---BPT Model
—BAT Model

(1) Recycle rate of 96% at BPT increased to 98% at BAT

TABLE 2. MODEL FLOW, EFFLUENT QUALITY, AND EFFLUENT LIMITATIONS AND STANDARDS

Ironmaking Subcategory (Blast Furnace)*

Model Size Plant: 6,000 TPD, 365 days/yr., 3 turns/day

	BPT (BAT, feed)		BAT-Alternative 4	Selected by EPA
Flow, gal/ton	125		70	
pH, units	6 to 9		6 to 9	
Pollutant:	Concentration, mg/L	lb/1000 lb	Concentration, mg/L	lb/1000 lb
Ammonia				
Average*	103	0.0535	10	0.00292
Maximum**	309	0.161	30	0.00876
Total Cyanide				
Average*	15	0.00780	1	0.000292
Maximum**	45	0.0234	2	0.000584
Phenols (4AAP)				
Average*	4	0.00210	0.1	0.0000292
Maximum**	12	0.00630	0.2	0.0000584
Suspended Solids				
Average*	50	0.0260	15	NA
Maximum**	150	0.0782	40	NA
Residual Chlorine				
Average*	NA	NA	NA	NA
Maximum**	NA	NA	0.5	0.000146

* Average of daily values for 30 consecutive days
** Maximum for any one day
NA:Not applicable

As the wastewater leaves the first reactor, acid is added to lower the pH to ∿8.5. Additional chlorine is added to the second reactor (second stage) to complete the oxidation of the cyanate, as well as the other pollutants, ammonia and phenols (breakpoint chlorination). The effluent is then dechlorinated with an appropriate reducing agent, such as sulfur dioxide, to remove the residual chlorine. BAT alternative 5 includes the use of activated granular carbon for the removal of residual levels of toxic organic pollutants which may be present in the effluent of BAT alternative 4. This was investigated on both pilot and full scale plants at the U.S. Steel, Gary Works.(1) The EPA selected BAT-4 on the basis that this treatment provides nearly complete removal of the pollutants at a lower cost than BAT-5. Alternative 5 was not selected on the basis of high incremental costs and minimal additional pollutant removal over that provided by BAT-4. Thus, BAT-5 will not be discussed further in this paper.

Two limited pilot scale investigations were made to evaluate the applicability of advanced wastewater treatment methods for upgrading steel mill wastewaters to BAT levels. One of the studies was performed by the Environmental Research Center, Rexnord Inc.(11) The other pilot study to evaluate alkaline chlorination alternatives for blast furnace treatment was conducted by the Industrial Division of Metcalf and Eddy Inc.(12)

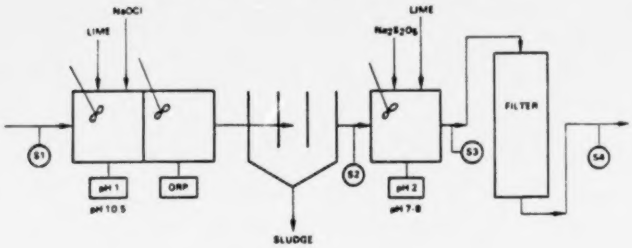
The Metcalf and Eddy study evaluated both a two-stage and a single-stage chlorination treatment system, Figure 6. Of the pollutant parameters that were monitored, ammonia and cyanide were the key parameters by which alkaline chlorination was evaluated.

Although effective removal of ammonia was reported by Metcalf and Eddy by both process alternatives, the two-stage process yielded more consistent levels. This can be attributed to a tighter control which the two-stage system has over the single-stage operation. The control of the operating pH in the second-stage was more favorable for ammonia and cyanate oxidation. It is equally important that the cyanates are oxidized, as well as ammonia, since cyanate first hydrolyzes to ammonia which is then oxidized to nitrogen.

Effective removal of the amenable cyanides (CN_A) was also reported by both treatment methods. There was a wide range of total cyanide (CN_T) levels present in the treated wastewaters. Some of the influent contained complex iron-cyanides, which are not amenable to chlorination, and therefore, were not oxidized in the process. Also of importance was the presence of organic priority pollutants, particularly the trihalomethanes (THM) which were formed during the chlorination process, Table 3.(12)

Construction and operating costs were estimated based on the treatment alternatives by Metcalf and Eddy. Costs were developed for treatment facilities to handle a blowdown rate of 300 gpm. This represents the EPA's model plant producing 6,000 tons of iron per day and a maximum blowdown rate of 70 gal/ton. The annual operating costs include chemicals, labor, power, and maintenance costs. Chemicals usage was estimated based upon results of the pilot plant operations and bench scale data. The influent was assumed to be BPT quality. The capital cost, amortized capital cost, and annual operating cost are summarized in Table 4. The treatment cost is very sensitive to chemical charges which represent 25 to 40 percent of the total cost.

1. SINGLE-STAGE ALKALINE CHLORINATION


NaOCl
LIME
Na2S2O5
LIME
FILTER
S1
S2
S3
S4
pH 1
ORP
pH 10.5
pH 2
pH 7-8
SLUDGE

2. TWO-STAGE ALKALINE CHLORINATION

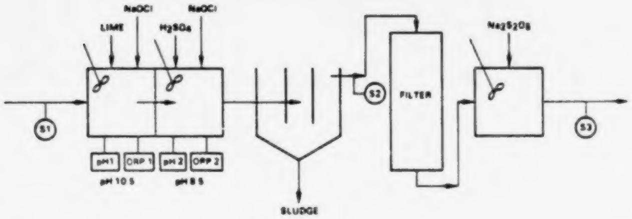

NaOCl
LIME
H2SO4
NaOCl
Na2S2O5
FILTER
S1
S2
S3
pH1
ORP 1
pH 2
ORP 2
pH 10.5
pH 8.5
SLUDGE

FIGURE 6 ALTERNATE PROCESS FLOW TRAINS (12)

TABLE 3. COMPARISON OF TRIHALOMETHANE DATA(12)

THM by Aikaline Chlorination Alternative	Influent (ppb)	Effluent (ppb)	
		Mean	Range
Single-Stage			
Chloroform	ND	750	530-1,000
Bromoform	ND	1,700	1,000-2,800
Dichlorobromomethane	ND	1,290	1,000-1,600
Chlorodibromomethane	ND	2,600	2,500-2,700
Two-Stage			
Chloroform	ND	28	11-40
Bromoform	ND	890	830-990
Dichlorobromomethane	ND	52	22-88
Chlorodibromomethane	ND	117	110-130

ND - Not Detected.

TABLE 4. COST COMPARISON(12)

	Alkaline Chlorination	
	Single-Stage	Two-Stage
Total Capital Cost	$1,202,000.	$1,235,000.
Amortized Capital Cost(1)	268,000.	275,000.
Annual Operating Cost	285,000.	296,000.
Total Annual Cost	$ 553,000.	$ 571,000.
Total Cost ($/1000 Gal)	3.60	3.72
($/ton)	0.25	0.26

(1)Amortized Cost at 18 for 10 years

TABLE 5. BAT-4 TREATMENT MODEL COSTS - IRONMAKING(1)

Model Size 6,000 TPD; 70 Gal/Ton, Basis 7/1/78 Dollars

Control & Treatment Technology Step	BAT Alternative-4			
	I	K	L	Total
Investment ($ X 10^{-3})	236.0	463.0	85.1	784.1
Annual Costs ($ X 10^{-3})				
Capital	21.2	41.6	7.7	70.5
Operation & Maintenance	8.3	16.2	3.0	27.5
Land	0.1	0.2	0.1	0.4
Sludge Disposal	2.8			2.8
Energy & Power	1.0	6.4	1.1	8.5
Chemical		123.8	2.9	126.7
Total Annual Cost	33.4	188.2	14.8	236.4
Cost				
$/Ton of Iron				0.11 (0.08)*
$/1,000 gallons W.W.				1.54 (1.08)*

*Total cost less capital investment cost

Key to C & TT

I: Inclined Plane Separation
K: 2-Stage Chlorination
L: Dechlorination - SO_2

TABLE 6. COMPARISON OF INDUSTRY AND EPA MODEL CAPITAL COST ESTIMATES(14) FOR IRON MAKING SUBCATEGORY (BAT-4)

		Capital Cost, 1978 Dollars		
Company	Basis for Company Estimates	Industry Model Estimates	EPA Model Estimates	Ratio Industry to EPA
U.S. Steel Corp.	Actual facility	$4,600,000	$820,000	5.6
BS Corp.	Site specific engrg. est.	$3,940,000	$820,000	4.8

COST COMPARISON

The EPA has stated that on the basis of the data collected the BPT effluent limitations promulgated in 1974 for blast furnaces utilizing recycle of process waters are practicable and achievable.(1) This technology has been installed by the iron and steel industry and an A. D. Little study(13) indicates that the toxic pollutants present in the wastewater are reduced by 99.04 percent.

The EPA selected BAT alternative 4 as the basis for the effluent limitations. The construction and treatment technology cost estimates, as determined by the Agency, are listed on Table 5. The cost estimate for BAT-4 is $1.54 per 1,000 gallons of wastewater treated (basis - 7/78 dollars), this cost increases to $2.31 per 1,000 gallons based on 7/83 dollars (using the Engineering News Record factor of 1.503).

The steel industry has taken issue with the cost estimates of the EPA and suggests that they are underestimated by a factor of at least 3. The industry contends that the EPA failed to take into account several factors such as, site-specific costs, allowances for cost escalation and working capital. For example, the EPA's estimated capital investment costs for BAT-4 was $820,000. However, based on the actual cost of a recently completed full scale facility, the estimated cost of the EPA's Model should be 4.6 million, or almost 6 times the EPA's estimate, see Table 6.(14)

Although these cost estimates are not in agreement, they do show that the cost of installing BAT-4 is high for the small incremental removal of pollutants achieved over the BPT processes. For example, the A. D. Little study shows that 99.04 percent of the toxic pollutants in the raw wastewater are removed by BPT controls, whereas a 99.89 percent reduction was estimated by installation of the BAT-4 controls. Thus, the difference in pollutant reduction by the addition of expensive BAT controls is only 0.85 percent.

In summary, some problems and limitations of the chlorination process are:

1) The high capital and operating costs.

2) Chlorination will not destroy the complex iron cyanides which may be present in varying amounts in blast furnace wastewater. This limitation can preclude compliance with the total cyanide standard.

3) Generally, toxic chlorinated organic compounds are formed, e.g., trihalomethanes, chlorophenols, and other chloroorganics. They may require additional treatment for their removal.

4) The addition of chlorine and pH adjusting chemicals significantly increase the level of dissolved solids in the treated wastewater.

5) Chlorine is a highly toxic chemical and can pose potential safety problems during transportation and handling. Also, if the reactions are not properly controlled, the toxic gas, cyanogen chloride, is formed and can evolve to pose a hazard to workers.

6) It has been reported that adequate control of the alkaline chlorination process is very difficult and requires constant attention to pH and ORP electrode operation.

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PHYSICAL-CHEMICAL CHARACTERIZATION OF BLAST FURNACE RECYCLE SYSTEM SCRUBBER WATER

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ABSTRACT

A research investigation is in progress to develop a better understanding of the chemistry and environmental engineering of blast furnace scrubber water systems. The approach entails field sampling and characterization activities with application of chemical concepts to understand precipitation, complexation, and adsorption. This information will be used to evaluate parameters which limit the extent to which scrubber water may be recycled, as well as to evaluate the effect of aqueous phase-suspended solid interactions on the fate of lead and zinc. These results will help to provide a rational basis for selecting and operating appropriate control technologies for efficient recycle of blast furnace scrubber water and for satisfying effluent limitation requirements.

INTRODUCTION

The purpose of this project is to develop an understanding of the chemical reactions and processes which occur in a blast furnace scrubber water recycle system. The study includes field sampling programs, laboratory characterization studies, and chemical modeling activities. The object of this work is to bring knowledge regarding blast furnace scrubber water chemistry to problems of water recycle and discharge of blowdown. This knowledge will help to improve management of blast furnace scrubber water with respect to issues that constrain the degree to which scrubber water may be recycled, as well as to problems of chemical speciation and reaction in blowdown water which impact the effluent quality of discharge from scrubber water recycle systems.

This paper presents a synopsis of the research methodology and progress for the investigation. The paper begins with a brief description of relevant background information and literature, this is followed by a discussion of scope of work. Some of the experimental findings from this study are presented to provide information on results from field studies, characterization of aqueous and solid samples, and laboratory studies. Chemical modeling activities are described, as well as directions for current and future research activities.

PREVIOUS INVESTIGATIONS

Recent commentaries on current blast furnace recycle scrubber water systems cover a wide range of issues. It is evident from a review of the literature that no clear consensus exists regarding definition of the most significant problem for management of blast furnace scrubber water, nor is there consensus on critical information needs for particular scrubber water management strategies. The following discussion shows that previous investigations have focused either on issues regarding treatment of blowdown from recirculating water for purposes of satisfying effluent limitations, or on issues related to treatment of recirculating water for purposes of preventing scale formation and deposition. The majority of previous studies have addressed problems of treatment and control technology for discharges from blast furnace scrubber water systems in order to meet environmental regulation. At present, the industry is addressing questions concerning the most cost effective methods to achieve compliance with the regulations defining Best Available Technology (BAT) (Wong-Chong and Caruso, 1978; Hofstein and Kohlmann, 1982). The BAT regulations include control of lead and zinc, as well as stringent control for ammonia, total cyanide and phenolics (46 FR 1858, Jan. 7, 1981).

Several investigations have evaluated biological treatment of blast furnace scrubber water. These investigations have taken divergent approaches and this is indicative of the lack of agreement regarding the appropriateness of biological treatment for control of contaminants in blast furnace scrubber water discharge. Gauthier, et al. (1981) performed bench tests to evaluate biological treatment of combined coke plant wastewater and blast furnace recycle water system blowdown. They reported that the particular blast furnace blowdown wastewaters employed in their studies were not toxic to the microbial population in a coke plant activated sludge process, and that the blast furnace water could be treated by combining it with coke plant wastewater. Krupinski and Damon (1982) describe the use of an attached growth biological treatment system for blowdown wastewater for conversion of ammonia to nitrate. This work showed that rotating biological contractors can be used successfully at pilot scale to reduce ammonia-nitrogen from about 300 ppm to less than 1 ppm. The attached growth process was used because of the relatively low biological strength characteristics of the blast furnace wastewater. This technology is being viewed by the U.S. Steel researchers as a candidate for the treatment of recycle blowdown wastewaters.

Various physical-chemical technologies have been proposed for treatment of blast furnace wastewaters. Federal Guidelines suggest that alkaline chlorination is considered a candidate best technology for cyanide control, however this technology is by no means widely used in the industry. For example, Tureck and Alton (1980) describe a full-scale treatment process which employs air stripping for ammonia removal with provision for treatment of phenol by oxidation with permanganate. Osantowski and Hendricks (1980) conducted pilot-scale tests to evaluate treatment of blast furnace water by combinations of physical-chemical technologies including: chlorination, ozonation, chemical precipitation, granular activated carbon adsorption and reverse osmosis. They judged that trains incorporating either alkaline chlorination, ozonation, or reverse osmosis were effective in meeting effluent requirements with the treatment train comprised of alkaline chlorination, chemical treatment and granular activated carbon adsorption being the least costly physical-chemical treatment alternative. Terril and Neufeld (1983) reported results of short-term laboratory tests to assess reverse osmosis treatment of blast furnace scrubber water. It was envisioned that permeate would be recycled to the scrubber water system with the reject stream receiving additional treatment. A cellulose acetate membrane was selected for use in the studies in part because the membrane displays poor rejection for cyanide and phenol at pH values below 7.0. It was believed that some mechanism existed in gas-scrubber recycle systems which would reduce the levels of cyanide and phenol if these contaminants were recycled to the scrubber water system.

Investigations on chemical treatment of blast furnace water have examined techniques to reduce formation of ferrocyanide and approaches for control of discharge of heavy metals. Prober et al. (1976) discussed treatment of blast furnace scrubber water to inhibit formation of iron-cyanide complexes. Proposed treatment schemes included oxidation of ferrous iron to the less reactive ferric iron or the use of copper or EDTA as competing ligands by sequestering ferrous iron with EDTA and cyanide with copper. Fitzpatrick et al. (1981) performed jar tests to evaluate trace metal removal from blast furnace scrubber blowdown by addition of ferrate (FeO_4^{2-}). Ferrate is a strong oxidant in which ferrate is reduced to ferric iron. Metal removal by use of ferrate may be achieved by a combination of: (i) adsorption in ferric-oxyhydroxide precipitate, (ii) heterocoagulation between $Fe(OH)_3$ and trace metal colloid, or (iii) sweep-floc removal of metal colloid.

Studies on treatment of blast furnace recirculating scrubber waters have focused on problems of scale formation control, particularly with respect to $CaCO_3$ and $CaSO_4$. Lange-Kennedy et al. (1982) proposed the use of a modified marble test to evaluate the $CaCO_3$ scaling tendency of blast furnace scrubber water. Although this approach was empirical, it would provide an indication of $CaCO_3$ scaling potential if the test were executed correctly and properly interpreted. The technique may be attractive for use in evaluating system performance where proprietary chemical additives are used as scale inhibitors. Brower et al., (1977) performed jar tests to evaluate the problem of control of $CaCO_3$ scale by treating blast furnace scrubber water with pickle liquor to remove calcium as $CaSO_4$; and the problem of scale formation in steel plant water recycle systems motivated St. Pierre and Khan (1981) to perform tests to learn more of $CaCO_3$ scale structure and growth rate.

Constraints on the degree to which blast furnace scrubber water may be recycled are not well understood. Without experimental data to verify his ideas, Crosbie (1979) believes that recycle systems can be tightened to less than one percent blowdown if indirect cooling systems replace the more typical open evaporative cooling systems. His idea centers on maintaining a higher partial pressure of CO_2 in the system in order to increase calcium carbonate solubility. In contrast, Hofstein and Kohlmann (1982) report on the foreign practice of aerating recirculating water to reduce the partial pressure of CO_2 in order to enhance carbonate precipitation. This practice of CO_2 expulsion occurs to varying degrees in most U.S. systems, depending on location of any acid addition, because of the presence of open clarifiers and open cooling towers.

Control of plugging and precipitation in most U.S. recycle systems is facilitated by the level of volumetric blowdown, by the addition of inorganic acids like HCl, and by the addition of proprietary chemicals for both corrosion and scale control. Current work at Republic Steel assessed a technology based on creating a split stream that is softened by the addition of caustic (Wisniewski and Nemeth, 1982). A "water softening" approach was also proposed by Elder and Littlewood (1981) for control of zinc-type scale deposits in blast furnace scrubber water recirculation system.

STUDY APPROACH

Our concept of the best direction for future blast furnace scrubber water research addresses the apparent need to enhance the chemical and environmental engineering knowledge base of these systems. Rather than develop a smorgasbord of add-on treatment units, we believe there is much to be gained in more clearly establishing the physical-chemical basis for choosing between alternative control strategies. For these reasons our work emphasizes development of knowledge regarding chemical speciation in blast furnace scrubber water and identifying changes that may occur in the principal unit operations of a blast furnace scrubber water recycle system. We are most interested in: (i) describing the composition of blast furnace recycle scrubber water, (ii) evaluating the change in the chemistry of the system as a result of passage through units which are open to the atmosphere and closed to the atmosphere, and (iii) assessing the potential for liquid-solid interactions to affect apparent solubility of selected species.

The basis for this investigation focuses on an understanding of the chemical interactions and processes which occur in a blast furnace scrubber water recycle system. The approach is outlined as follows:

1. The concepts of chemical equilibrium are being applied to the blast furnace scrubber water recycle system. A sufficiently detailed approach is being undertaken in order to adequately understand the roles of chemical precipitation and chemical complexation, and to identify the significance of surface adsorption with respect to the heavy metals regulated under BAT Guidelines (viz. lead and zinc). The procedure involves the transfer of techniques which have been used successfully to describe chemical speciation in natural water systems and in electric power generating effluents (Westall, et al. 1976; Benjamin, et al. 1982; EPRI, 1982).

2. The study will begin to develop an understanding of chemical equilibria relationships in view of blast furnace gas quality and scrubber water quality. It is of special interest to note that essentially no published data exists with regard to the quality of blast furnace gas for constituents of environmental importance. The approach to be taken entails formulation of a methodology from which a process model may be constructed. Not all elements of the model will be addressed in the investigation, as the principal tasks for this study pertain to recycle water characterization and interpretation of chemical data.

3. The investigation is evaluating the importance of particle separation and selected solid phase chemical reactions with respect to environmental control. This is being achieved by characterization of the physical and chemical properties of solids, and by evaluating the tendency for lead and zinc to adsorb onto solids.

4. The study will investigate parameters which limit the extent to which scrubber water may be recycled. This will be achieved by conducting chemical concentration tests in conjunction with chemical equilibria modeling. The role of chemical complexation is particularly important in evaluating the tendency for blast furnace scrubber water to scale. This will be studied by investigating the impact of ligands naturally occurring in the scrubber water, as well as by evaluating the impact of sequestering

agents which may be added to scrubber water. The latter activities will address the use of chemically well-defined sequestering and chelating agents, rather than proprietary additives in order to facilitate understanding.

PROGRESS TO DATE

Research progress has been made in the following areas: (1) field sampling program, (ii) water and solids characterization, (iii) laboratory studies on behavior of lead and zinc, and (iv) development of chemical and process models. Each of these topics are discussed below.

Field Studies

The purpose of the field sampling program is to provide a data base for a blast furnace scrubber water recycle system. Arrangements were made with a Pittsburgh-area steel corporation to conduct a field sampling program on an operating blast furnace scrubber water recycle system. This wastewater control system was recently constructed and has been in operation for approximately one and a half years. The scrubber water recycle system is illustrated in Figure 1, which shows two blast furnaces with associated gas scrubber and gas cooler. Waters from the blast furnace gas (BFG) scrubbers are combined, aerated, and treated by the addition of anionic polymer. The purpose of the aeration is to provide mixing and control CO_2, while the purpose of the polymer is to aid suspended solid removal during clarification. Solids removed in the clarifier are dewatered by vacuum filtration with the cake being sent to the sintering plant, and the filtrate being returned to the clarifier. Overflow from the clarifier is combined with gas cooler water in the hot well. Make-up water is added in the cold well, and discharge from the cold well is recycled to the gas scrubbers and coolers while system blowdown is taken from the recycle water. The system is designed to permit the use of chemical flocculants to be added to the flow before clarification. The addition of acid in the hot well is designed for pH control, and descalents may be added at the cold well following the cooling tower.

Figure 1 identifies the locations of sample points for the collection of water and solid samples, and a comprehensive sampling program of the type illustrated in Figure 1 has been completed with the collection of composite water and solid samples from the indicated locations. Aqueous samples were fractionated and preserved according to the scheme outlined in Figure 2. A second sampling program focused on collection of additional solid samples and collection of composite samples of combined gas scrubber water prior to aeration and following clarification.

Characterization of Blast Furnace Recycle Water

The system described in Figure 1 employs a recirculating, or recycle, flow of nominally 6000 gpm, blowdown is about 140 gpm, and make-up water is less than 500 gpm. Water is lost from the system via the filter cake (less than 10 gpm), humidification of the BFG (about 160 gpm), and by evaporation and drift from the cooling towers (about 275 gpm). The blowdown flow is approximately 2% of the recirculating flow. Hydraulic residence time in the system is about 150 minutes based on about 5 minutes in the venturi scrubber and spray cooler sump, 1 minute in a flash mixer, 134 minutes in the clarifier, 5 minutes in the hot well, and 5 minutes in the cold well. These times are based on the actual or design flows through the units. Nominally 90 percent of the hydraulic residence time occurs in the clarifiers.

At maximum flow rate, the clarifier will allow a minimum of 65 minutes residence time.

Table I is a summary of water quality measurements for selected days between September 1982 and January 1983 for the blowdown stream. Table II is a summary of water quality measurements from field sampling activities for make-up water, influent and effluent water from the clarifier, hot well and cold well water from the cooling tower, and blowdown water, while Table III is a comparison of major cations and anions for makeup and blowdown water. Table IV is a summary of water quality data collected from a second field sampling activity. The sampling program was limited to developing a more detailed characterization of water quality at the clarifier. Table IV represents a short time series profile of clarifier influent and effluent over about a 5 hour interval. Table V compares major cations and anions in clarifier influent and effluent. It is recognized that the concentration values reported in Tables I, II and IV for CN, NH_3, and phenolics are low for this system in comparison with typical values reported in the literature.

It is apparent that water quality throughout the scrubber system, as represented by our sampling locations, is relatively uniform with the exception of the change in suspended solids across the clarifier and water temperature across the cooling tower. It is important to note that there is an appreciable change in water quality between the make-up water to the system and the blowdown. These changes in water quality are the result of two mechanisms : (1) a consumptive or evaporative water loss due to humidification of the BFG and evaporative loss in the cooling tower, and (2) a pickup of dissolved chemicals and suspended solids from the cleaning of the BFG. It appears that nearly a four-fold increase in concentration of conservative chemicals, such as TDS, hardness, and sodium, can be attributed to evaporative concentration effects. Some chemicals, namely potassium, magnesium, ammonia-N, fluoride, and chloride, demonstrated an increase in concentration due to evaporative effects, as well as further increase due to mass pickup from the BFG. Potassium shows a total increase of more than 150 times while fluoride and ammonia-N increase in concentration between 75 and 100 times.

Because our water quality measurements indicate that the chemical concentration of many constituents do not vary appreciably around the system, we may conveniently model the blast furnace scrubber system in terms of describing the collection of process units and environmental control units as a single, complete-mix reactor system. Figure 3 shows the configuration for the mathematical model. This model is based on the premise that the water quality concentration within the system is identical to the concentration in the blowdown, the cooling water drift, and the filter cake water.

The model predicts that steady state concentration, C_∞, is given by:

$$C_\infty = C_I(Q_I/Q_o) + (m/Q_o) \qquad \text{(Eq 1)}$$

where C_I is the concentration in the make-up water, Q_I is volumetric flow rate of the make-up water, Q_o is the total water loss rate for those streams that carry away dissolved chemicals, and m is the mass rate of chemical pickup from the BFG scrubbing process. Note that Q_I is larger than Q_o because of the need to provide make-up water that is lost by evaporation or gas humidification.

Equation 1 may be rewritten in the form:

$$C_\infty/C_I = (Q_I/Q_o) + (mQ_o/C_I) \qquad \text{(Eq 2)}$$

The term (C_∞/C_I) is sometimes called the number of cycles of concentration in the cooling tower literature. The term (Q_I/Q_o) is the ratio of the make-up water rate to the water loss rate which represents the cycles of concentration due to evaporative effects. If there is no mass pickup due to BFG cleaning (i.e. $m=0$) then we expect in steady state that the cycles of chemical concentration (C_∞/C_I) is identical to (Q_I/Q_o). This is true for some species in the blast furnace system, but for other chemicals, the mass pick-up term is the principal contributor to the change in water quality.

Table VI summarizes our data comparing the water quality of the blowdown with the make-up water to show the ratio of blowdown concentration to make-up concentration. The data range from about 160 for potassium to about 3 for sulfate and TDS. It is estimated that the ratio of make-up water flowrate (Q_I) to water loss rate (Q_o) is about 3 to 4 for these data. We do not have extensive enough water flow data to be more precise regarding the ratio of (Q_I/Q_o) at this time. The additional cycles of concentration above 4 for the other chemicals listed in Table VI reflects the mass pickup per pass for the recycled water.

The simple model lets us predict some other characteristics of the recycle system. The concentration of chemicals in the recycle water vary with time as

$$C(t) = C(t=o) \times \exp\,[-Q_o t/V] + [(Q_I C_I + m)/Q_o] \times [1 - \exp(-Q_o t/V)] \qquad \text{(Eq 3)}$$

From this solution, the time to come to 99 percent of steady state concentration is estimated as

$$t_{99} = 4.6\ t_o = 4.6\ (V/Q_o) \qquad \text{(Eq 4)}$$

where t_o is the hydraulic residence time for the complete-mix model which can be expressed as the ratio of the volume of the reactors in the system (V) divided by the water loss rate (Q_o). The volume in the system is principally the volume of the water in each clarifier, about 250,000 gallons, but there is additional storage volume provided in the hot and cold wells and the spray cooler pump, about 30,000 gallons each. The residence time, t_o, is estimated to be about 2125 minutes based on Q_o equal to 160 gpm and V equal to 340,000 gallons. The time for the system to reach near steady state, t_{99}, is then about 9800 minutes, or more than 7 days. Practically, this means that major changes in the system, such as shutting down the furnaces (i.e. $m=0$) while keeping the recycle system running ($Q_I \neq 0$, and $Q_o \neq 0$), will produce changes that take several days to come to a new steady condition. This pattern suggests that sampling on a Monday after a shut-down weekend will produce different results than one would get on a Thursday or Friday.

Solids Characterization

Blast furnace flue dust was categorized into two classes for characterization purposes: (i) dry dust solids removed from the dry dust catcher, and (ii) filter cake solids representing dewatered solids removed by the venturi scrubber. Laboratory experiments were conducted with one composite sample of dry dust solids and two samples of filter cake solids obtained in separate sampling trips. For some analyses the solids were separated into fine size fraction and coarse size fraction.

Solid characterization activities include physical descriptions, mineralogic determinations, and chemical behavior interpretations. Sieve analysis of the samples indicated that particle sizes ranged from microns to several millimeters; approximately one third to one half of the filter cake solids were finer than 74 microns (No. 200 sieve) and mean particle diameter for the filter cake solids was 0.2 mm. An estimate of surface area determinations showed that filter cake solids and the dry dust solids had surface areas in the range of 10 to 40 m^2/g. X-ray diffraction analyses were performed on the solid samples in order to identify major crystalline components. The filter cake solids showed that Fe_2O_3 and Fe_3O_4 were major components. The fine fraction (< No. 200 sieve) dust catcher solids also showed these two compounds as major components, but the coarse fraction (> No. 40 sieve) dust catcher solids were comprised almost entirely of amorphous material. Both the dry dust catcher solids and the filter cake solids were found to possess very high acid neutralizing capacities. The fine fraction of filter cake solids and dry dust solids demonstrated acid neutralizing capacities of approximately three milliequivalents per gram, while the coarse fraction of each solid gave one to two milliequivalents per gram. Additional work is in progress to evaluate the leach characteristics of the solids in order to assess the tendency for the solids to release heavy metals. Additional characterization is also being performed to examine the metal composition of particles by scanning electron microscopy with energy dispersive analysis by X-rays (SEM/EDAX).

Laboratory Studies on Behavior of Lead and Zinc

Several investigators have shown that heavy metal adsorption occurs to varying degrees on oxide particles. The extent of adsorption depends on various factors including metal specie and oxidation state, pH, competition from other adsorbents, the presence of other adsorbates, ionic strength, and the surface characteristics of the oxide. Recent literature has shown the importance of understanding surface adsorption reactions in order to explain the behavior of heavy metals in aqueous solution in the presence of iron oxyhydroxide surfaces (Benjamin, et al. 1982 and references contained therein).

Laboratory experiments were performed with solutions containing dry dust catcher and filter cake solids to observe the response in lead and zinc concentration to change in pH. The experiment consisted of placing five grams of each solid in 100 ml 0.1 N $NaClO_4$ solution, adding acid, mixing, recording pH value, centrifuging and measuring total soluble lead and zinc in the supernatant by either flame or flameless atomic absorption. Representative results with zinc are presented in Figure 4 which shows that zinc concentration in acidified samples is more than 100 mg/l. As pH is increased, zinc is removed from solution particularly over the pH range 6 to 7. The removal of zinc is greater than can be explained in consideration of simple $Zn(OH)_2$ solubility product. Chemical modeling activities are in progress to aid interpretation of the data displayed in Figure 4, particularly with respect to carbonate chemistry.

Data shown in Figure 4 demonstrate that soluble zinc concentration is dependent on solution pH value. The sensitivity of the zinc concentration to the solution pH is particularly important when it is noted that NPDES guidelines permit the effluent pH to be anywhere in the range 6-9 for compliance. Additionally, there is an indication that recycle systems are often designed to stay at the low end of the pH range to reduce a tendency for scale formation.

Additional work is planned to observe lead and zinc solubility as a function of pH and solids concentration. These results will be interpreted with aid of a chemical equilibrium model in order to differentiate between removal of heavy metal by chemical precipitation and removal by adsorption on solids. This analysis will permit development of metal-solid isotherm parameters.

Chemical Modeling Developments

The purpose of the chemical modeling effort is to provide estimates of the distribution, speciation, and fate of dissolved constituents and precipitated solids in blast furnace scrubber water recycle system. Work to date has focused on modification of an existing chemical equilibrium computer model with application to understanding speciation of constituents in field samples and in laboratory tests.

The chemical equilibrium model selected for this project was MINEQL (Westall, et al. 1976). Modifications were made to MINEQL in order to adapt the program to describe chemical composition of blast furnace scrubber waters. These modifications included the addition of a temperature correction for formation constants, an ionic strength calculation, an electro-neutrality check, and the addition of a gas-liquid ammonia equilibrium constant to the data base. Also, a user interface was incorporated to allow a more dynamic interaction between the user and the program.

The program has been used to begin assessment of the affects of changes of temperature and partial pressure of carbon dioxide on precipitation of solids and on changes in process water chemistry (Luthy, et al. 1983). This is useful for evaluating if scrubber water is supersaturated with respect to potential scale-forming solids and for evaluating speciation of metals of environmental importance. As mentioned above, the chemical equilibrium model is also being employed to interpret the extent to which lead and zinc may form hydroxide and carbonate solids and other species, including interaction with blast furnace iron oxide solids.

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Notice

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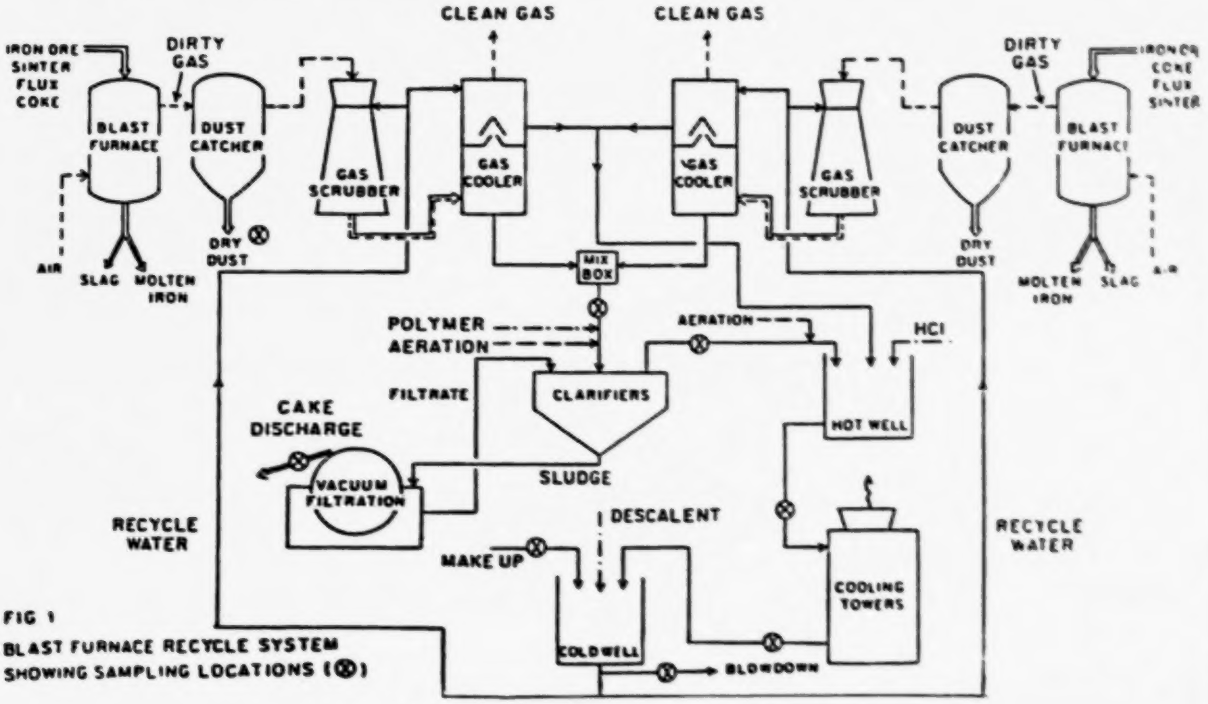
CLEAN GAS
CLEAN GAS
IRON ORE
SINTER
FLUX
COKE
DIRTY GAS
BLAST FURNACE
DUST CATCHER
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GAS COOLER
GAS COOLER
GAS SCRUBBER
DUST CATCHER
BLAST FURNACE
DIRTY GAS
IRON ORE
COKE
FLUX
SINTER
AIR
SLAG
MOLTEN IRON
DRY DUST
MIX BOX
DRY DUST
MOLTEN IRON
SLAG
AIR
POLYMER
AERATION
AERATION
HCl
FILTRATE
CLARIFIERS
HOT WELL
CAKE DISCHARGE
VACUUM FILTRATION
SLUDGE
RECYCLE WATER
DESCALENT
RECYCLE WATER
MAKE UP
COOLING TOWERS
COLD WELL
BLOWDOWN

FIG 1
BLAST FURNACE RECYCLE SYSTEM
SHOWING SAMPLING LOCATIONS (⊗)

FIG. 2
FRACTIONATION AND PRESERVATION OF SCRUBBER WATER SAMPLES

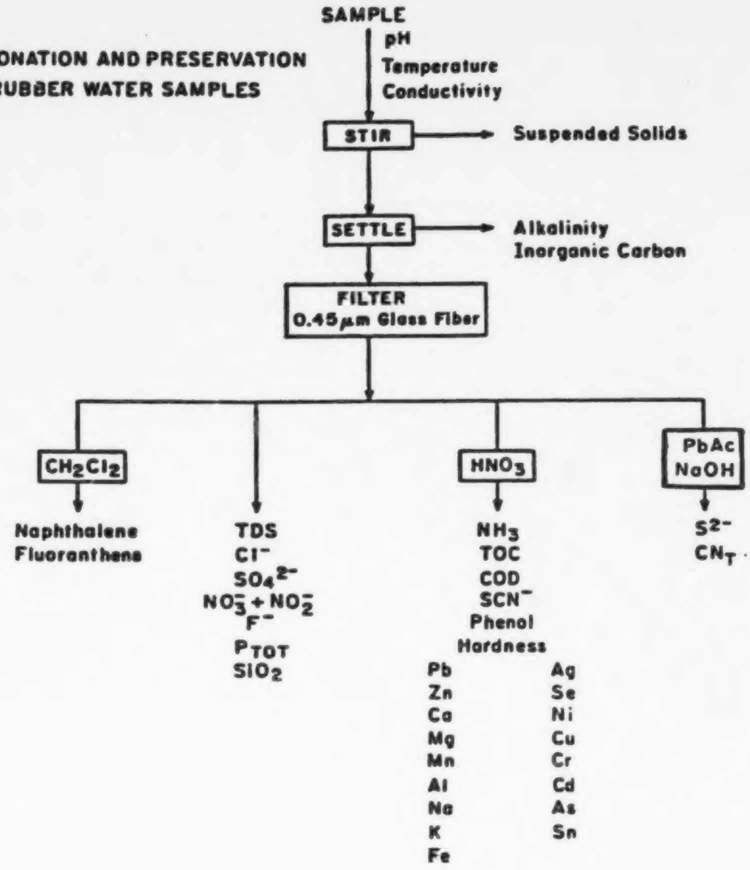
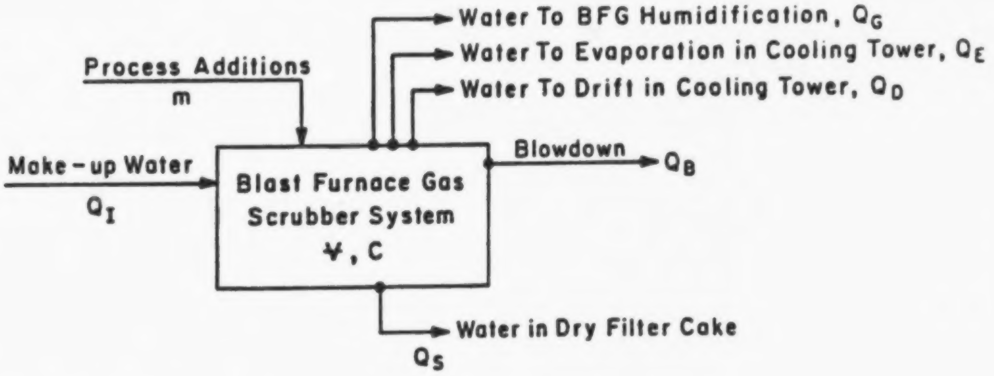

SAMPLE
pH
Temperature
Conductivity
STIR
Suspended Solids
SETTLE
Alkalinity
Inorganic Carbon
FILTER
0.45μm Glass Fiber
CH2Cl2
Naphthalene
Fluoranthene
TDS
Cl−
SO4 2−
NO3− + NO2−
F−
P TOT
SiO2
HNO3
NH3
TOC
COD
SCN−
Phenol
Hardness
Pb
Zn
Ca
Mg
Mn
Al
Na
K
Fe
Ag
Se
Ni
Cu
Cr
Cd
As
Sn
PbAc
NaOH
S2−
CN T

FIG. 3
CONFIGURATION FOR MATHEMATICAL MODEL OF BFG SCRUBBER WATER RECYCLE SYSTE


Water To BFG Humidification, Q G
Water To Evaporation in Cooling Tower, Q E
Water To Drift in Cooling Tower, Q D
Process Additions
m
Make-up Water
Q I
Blast Furnace Gas
Scrubber System
V, C
Blowdown
Q B
Water in Dry Filter Cake
Q S

Water Balance Equation

$$\frac{d\mathcal{V}}{dt} = Q_I - Q_S - Q_B - Q_G - Q_E - Q_D$$

Chemical Balance Equation

$$\frac{d(C\mathcal{V})}{dt} = Q_I C_I + m - Q_S C_S - Q_B C_B - Q_D C_D$$

Steady State

$$\frac{d\mathcal{V}}{dt} = 0 \quad Q_I = Q_S + Q_B + Q_G + Q_E + Q_D$$

Call $Q_O = Q_S + Q_B + Q_D$

$$\frac{d(C\mathcal{V})}{dt} + C(Q_S + Q_B + Q_D) = Q_I C_I + m$$

$$\text{or } \mathcal{V}\frac{dC}{dt} + Q_O C = Q_I C_I + m$$

FIG. 4 LABORATORY STUDIES ON BEHAVIOR OF ZINC

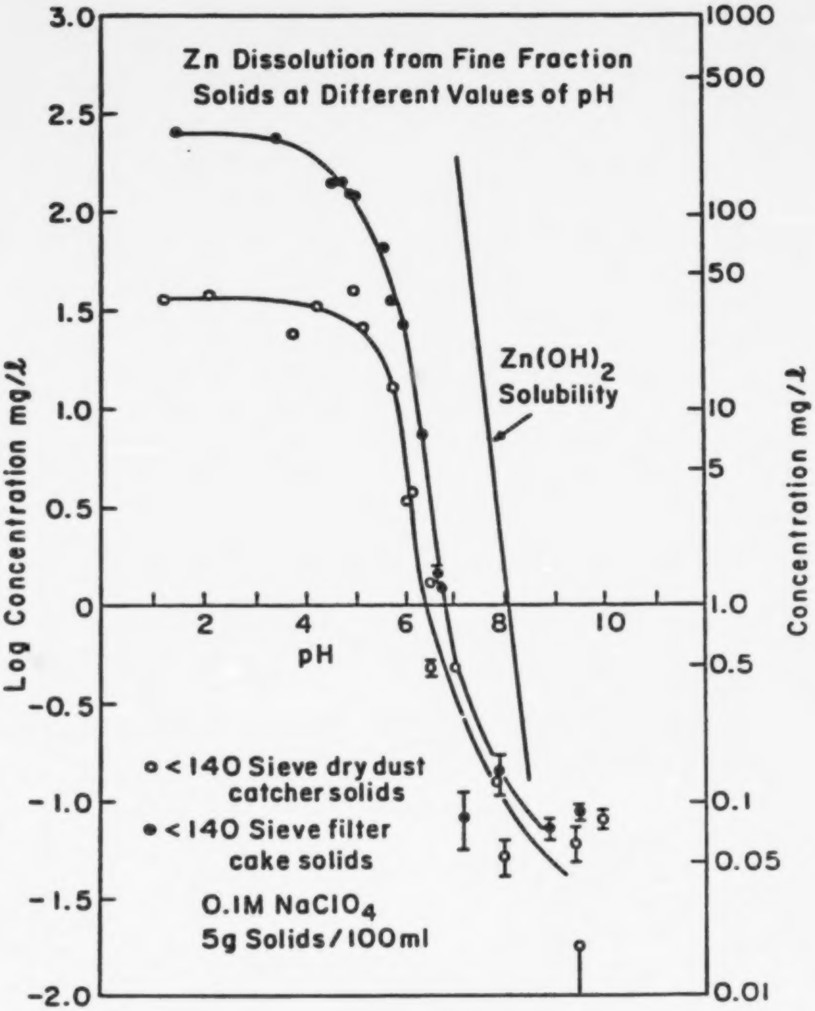


Table I

WATER QUALITY FOR BLOWDOWN

COMPANY DATA-SELECTED SAMPLES DAILY SEPTEMBER 1982-JANUARY 1983

Characteristic	No. of Samples	Mean	S.D.	UNITS
Recirculation Rate	25	6420	483	gpm
Blowdown Rate	26	140	25	gpm
Percent Blowdown	25	2.25	0.29	%
pH	26	7.3	0.3	S.U.
Temperature	26	92	5	°F
TSS	23	17	11	mg/L
TDS	17	1246	165	mg/L
NH_3-N	25	29	7	mg/L
CN-Total	25	<0.02	-	mg/L
Phenolics (4AAP)	25	54	31	mg/L
Ca Hardness (as CaCO3)	19	300	54	mg/L
Alkalinity (as CaCO3)	19	309	90	mg/L
Lead-Total	15	62	28	µg/L
Zinc-Total	15	467	151	µg/L

Table II

COMPARISON OF WATER QUALITY AT SELECTED LOCATIONS IN THE BFG SYSTEM

(All Concentrations, mg/l; mean ± Std. Deviation)

Major Constituents

		Clarifier		Cooling Tower		
Chemical	**Make-Up**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Blowdown**
SS	2 ±	367 ± 85	8 ± 3	13 ± 16	22 ± 14	10 ± 6
Alk. (as $CaCO_3$)	30.5 ±	270 ± 23	241 ± 30	238 ± 25	241 ± 24	232 ± 25
TDS	396 ±	1270 ± 14	1262 ± 54	1332 ± 192	1280 ± 11	1290 ± 94
TEMP (°C)	11.5 ± 1.7	51.4 ± 1.1	48.2 ± 1.5	47.1 ± 1.6	37.8 ± 4.7	32.1 ± 0.3
Cl^-	45 ± 0.3	440 ±	452 ± 18	462 ± 4	430 ± 7	435 ± 7
SO_4^{2-}	41.6 ± 1.9	99 ± 19	106 ± 24	114 ± 19	120 ± 5	122 ± 5
NO_2^-/NO_3^-	< 2 ±	8.9 ± 1.3	9.0 ± 0.1	11.1 ± 1.3	< 7 ± 7	-
F^-	< 0.1 ±	10 ± 0.1	9.8 ±	10 ± 0.1	9.9 ±	10 ±
NH_3-N	0.3 ±	22.8 ± 0.5	24.4 ± 0.5	23.0 ± 1.3	22 ±	22.5 ± 0.7
COND. (μM/cm)	187 ± 11	3138 ± 149	3070 ± 117	2812 ± 155	2531 ± 168	2226 ± 155
Mg	7.1 ±	66.2 ± 1.3	66.8 ± 2.0	65.0 ± 3.0	66.0 ± 0.8	64.1 ± 0.6
Na	12.7 ±	48.0 ± 2.1	50.0 ± 2.2	48.8 ± 1.4	49.4 ± 2.2	48.6 ± 1.9
Ca	26.2 ±	113 ± 1	112 ±	106 ± 3	110 ± 2	107 ± 1
K	1.9 ±	298 ± 37	304 ± 23	296 ± 20	303 ± 17	294 ± 18
COD	15 ±	93.5 ± 4.9	92.0 ± 2.8	84.5 ± 13.4	97 ± 0	82.5 ± 3.5
BOD	< 2	3.0 ± 0.8	< 3.4 ± 1.9	< 2.8 ± 1.1	3.0 ± 0	< 2.2 ± 0.3
TIC	6.2 ±	39.6 ± 4.0	36.2 ± 2.4	48.1 ± 13.1	43.2 ± 6.6	40.7 ± 3.4
TOC	3.9 ±	13.9 ± 4.2	17.9 ±	12.2 ± 1.8	15.2 ± 0.1	14.3 ± 1.4
pH (units)	7.17 ± .15	7.46 ± .10	7.60 ± .12	7.52 ± .02	8.02 ± .13	8.04 ± .04

Minor Constituents

		Clarifier		Cooling Tower		
Chemical	**Make-Up**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Blowdown**
Phenolics	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
CN-total	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Naphthalene	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
Fluoranthene	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
SiO_2-colloidal	< 0.17	< 1.9 ± 0.4	< 0.17	0.26 ± 0.03	0.24 ± 0.0	0.23 ± 0.09
SiO_2-soluble	2.6 ±	29.0 ± 1.4	30 ± 0	29.5 ± 0.7	29 ± 0	29.5 ± 0.7
SiO_2-total	2.6 ±	31.0 ± 1.4	30 ± 0	29.5 ± 0.7	29 ± 0	28.5 ± 0.7
P-total	0.06 ±	0.12 ± 0.04	0.06 ± 0	0.22 ± 0.01	0.09 ± 0.01	0.26 ± 0
Fe-total	0.26 ±	0.27 ± 0.04	0.05 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.08 ± 0.01
Fe^{2+}	< 0.05	0.10 ± 0.04	< 0.05	< 0.05	< 0.05	< 0.05
Zn	0.02 ±	1.27 ± 0.06	0.52 ± 0.01	0.36 ± 0.01	0.34 ± 0.01	0.34 ± 0.01
Pb	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Al	0.2 ±	0.80 ± 0.14	0.65 ± 0.07	0.65 ± 0.07	0.55 ± 0.21	0.55 ± 0.21
SCN	-	1.31 ± 0.08	1.31 ± 0.08	1.25 ± 0	1.25 ± 0	1.25 ±
S^{2-}	-	< 1	< 1	< 1	< 1	-
Sn	-	-	-	-	-	< 1
Ag	-	-	-	-	-	< 0.01
Se	-	-	-	-	-	< 0.02 ± 0.02
Ni	-	-	-	-	-	< 0.03
Cu	-	-	-	-	-	< 0.01
Cr	-	-	-	-	-	< 0.01
Cd	-	-	-	-	-	< 0.005
As	-	-	-	-	-	0.024 ± 0.003

Table III

MAJOR CATIONS AND ANIONS IN MAKEUP AND BLOWDOWN WATER

Chemical	MAKE-UP WATER		BLOWDOWN	
	Mean(mg/l)	Millieqv./l	Mean(mg/l)	Millieqv./l
TDS	396		1290	
K	1.86	0.05	294	7.52
Na	12.7	0.55	48.6	2.11
Ca	26.2	1.31	107.5	5.36
Mg	7.1	0.58	64.1	5.27
	sum	2.49	sum	20.26
Cl	45.0	1.27	435	12.27
SO_4	41.6	0.87	122	2.54
Alkalinity	30.5	0.61	232	4.64
F	<0.1	-	10.1	0.53
NH_3-N	0.3	0.02	22.5	1.61
	sum	2.77	sum	21.59

Table IV

STATISTICAL COMPARISON OF CLARIFIER WATER QUALITY

	CLARIFIER INFLUENT			CLARIFIER EFFLUENT		
Chemical	Number of Samples	Mean	SD	Number of Samples	Mean	SD
T (°C)	6	55.8	1.9	6	52.8	0.8
pH (units)	6	7.72	0.06	6	7.80	0.04
EC (μM/cm)	6	5917	254	6	5683	103
COD	3	53.5	2.5	3	59.1	5.7
TIC (as C)	3	162	5	3	162	3
TOC (as C)	3	47.4	4.1	3	56.0	1.9
Alkalinity (as CaCO3)	3	693	110	3	583	6
Al	3	0.7	0.2	3	< 0.2	0.1
Ca	3	137	6	3	120	0
Pb	3	< 0.06	0.04	3	< 0.03	-
Mg	3	96	3	3	93	2
Mn	3	2.96	0.39	3	2.65	0.12
K	3	923	57	3	827	76
Na	3	149	4	3	148	2
Zn	3	0.81	0.69	3	0.44	0.15
Fe-Total	3	1.36	0.29	3	1.10	0.03
Fe^{+2}	3	< 0.1	-	3	< 0.1	-
SCN	3	0.66	0.25	3	0.44	0.08
P	3	< 0.02	0.01	3	0.04	0.03
Cl	3	657	72	3	670	114
F	3	41.0	4.6	3	47.3	2.1
NO_3-N	3	< 0.2	-	3	< 0.2	-
NO_2-N	3	0.43	0.03	3	0.46	0.02
SO_4	3	317	46	3	250	35
NH_3-N	5	24.1	0.7	3	25.6	0.3
Silica-Total	3	34.7	0.6	3	34.7	3.2
Silica-Soluble	3	33.7	1.5	3	34.3	2.9
Silica-Colloidal	3	0.86	0.74	3	0.48	0.18
TDS	3	2252	3	3	2445	85
SS	3	2073	911	3	102	4
VSS	3	275	26	3	102	4

Note: Concentration as mg/l unless noted. Data are from second field trip.

Table V

MAJOR CATIONS AND ANIONS IN CLARIFIER INFLUENT AND EFFLUENT

(Second Field Trip)

	Influent		Effluent	
Chemical	**Mean(mg/l)**	**Millieqv./l**	**Mean(mg/l)**	**Millieqv./l**
TDS	2252		2445	
K	923	23.6	827	21.2
Na	149	6.5	148	6.4
Ca	137	6.8	120	6.0
Mg	96	7.9	93	7.6
	sum	44.8	sum	41.2
Cl	657	18.5	670	18.9
SO_4	317	6.6	250	5.2
Alk (as $CaCO_3$)	693	13.9	583	11.7
F	41.0	2.2	47.3	2.5
NH_3-N	24.1	1.7	25.6	1.8
	sum	42.9	sum	40.1

Table VI

CYCLES OF CONCENTRATION DATA

	Source		
Chemical	**Make-Up**	**Blowdown**	**Blowdown / Make-Up**
TDS (ppm)	396	1290	3.2
K (ppm)	1.86	294	160
Na (ppm)	12.7	48.6	3.8
Ca (ppm)	26.2	107.5	4.1
Mg (ppm)	7.1	64.1	9.0
Cl (ppm)	45.0	435	9.7
SO_4 (ppm)	41.6	122	2.9
Σ cations (meq)	2.49	20.26	8.1
Σ anions (meq)	2.77	21.59	7.8

REMOVAL OF TRACE ORGANIC CONTAMINANTS FROM COKE PLANT WASTEWATER AND BLAST FURNACE BLOWDOWN IN A BIOLOGICAL FLUIDIZED BED SYSTEM

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ABSTRACT

The removal of trace organic constituents from coke plant wastewater and blast furnace blowdown was evaluated over a two-year period in a pilot scale two-stage biological fluidized bed system. The treatment system was designed to evaluate the feasibility of nitrifying and denitrifying these wastewaters. In a parallel activity, the system was assessed for its capability of removing U.S. EPA organic priority pollutants and 24 organic base/neutral non-priority pollutants.

When treating coke plant wastewater alone, nine U.S. EPA base/neutral priority pollutants were identified at greater than trace concentrations (0.01 $mg \cdot L^{-1}$) in more than one untreated coke plant wastewater sample. These included polyaromatic hydrocarbons (PAHs) such as acenaphthylene, acenaphthene, anthracene/phenanthrene, fluoranthene, naphthalene and pyrene. Heterocyclic nitrogenous compounds (HNCs) such as isoquinoline, indole, carbazole and quinoline were consistently present at elevated concentrations. Only one base/neutral priority pollutant and one non-priority pollutant were identified at greater than trace concentrations in more than one sample collected after treatment in the biological fluidized bed process.

Only di-n-butyl phthalate was identified at greater than trace concentrations in the treated effluent from the combined wastewaters despite the presence of a range of trace organic pollutants at concentrations up to approximately 15 $mg \cdot L^{-1}$ in the raw wastewater. There appeared to be an accumulation of some PAHs including fluoranthene, pyrene and benzo(a)-anthracene/chrysene in the biological sludges.

INTRODUCTION

By-product coke plant wastewater and blast furnace scrubber blowdown water contain significant levels of toxic contaminants (1,2). The majority of the organic contaminants are base/neutral extractable compounds resulting from the destructive distillation of coal. Prominent organic contaminant groups in coke plant wastewaters include PAHs, phthalate esters, HNCs and phenolic compounds (1,3-6). Lower levels of phenolics and PAHs are found in blast furnace blowdown water (1).

Biological treatment of blast furnace blowdown is not commonly practised since the low concentration of organic contaminants is inadequate to support biological growth. Conversely, biological treatment of coke plant wastewaters is widely practised. Consequently, trace organic contaminant removal studies have generally been conducted on biological treatment schemes for coke plant wastewaters. Wilson et al (5) demonstrated that bench-scale activated sludge systems with and without powdered activated carbon (PAC) addition, operated at 60 day solids retention time (SRT) and 26 per cent dilution, could effect significant removals of organic priority pollutants. They concluded that PAC addition did not improve priority pollutant removal. Wong-Chong and Hall (4) confirmed biological removal of trace organic contaminants in bench-scale and full-scale activated sludge systems. They cited SRT as one of the critical process parameters for controlling organic priority pollutant removal. Pilot plant studies reported by Osantowski and Geinopolos (7) and Osantowski and Hendriks (8) indicated that biological treatment effectively removed all volatile, base/neutral and acid extractable organic priority pollutants to non-detectable levels.

In 1978, Environment Canada initiated a four-year program at their Wastewater Technology Centre (WTC) to develop a biological treatment technology that would nitrify and denitrify coke plant wastewater. Initially, work focussed on suspended growth systems. Bridle et al (6,9) operated bench-scale activated sludge reactors in the pre-denitrification nitrification mode at high SRTs and hydraulic retention times (HRTs) and with PAC addition. They showed that most organics present in coke plant wastewater were effectively removed from the aqueous phase. However, accumulation of PAHs, notably indeno-pyrene, naphthalene, pyrene and benzo-(a)-anthracene, occurred in the biological sludge. Also, HNCs such as 9H carbazole, 9H anthracene carbonitrile, indolizene and phenanthridine were concentrated in the sludge. Any enhancement of trace organic pollutant removal as a result of PAC addition could not be assessed in their work.

Subsequent work initiated in 1980 examined the feasibility of applying pre-denitrification nitrification technology in a fluidized bed mode. In the first phase of the fluidized bed work, 18 month pilot-scale trials of a two-stage fluidized bed system achieved a performance comparable to the suspended growth system examined by Bridle et al (6,9) but at the significantly reduced reactor HRT of 16 h and without wastewater dilution or PAC addition (10,11). In Phase 2, the treatment of a mixture of coke plant wastewater and blast furnace blowdown water was examined over a six-month period. Performance data comparable to Phase 1 were achieved but at the considerably reduced HRT of 4.5 h (12,13).

This paper reports on the ability of the biological fluidized bed system to remove trace organic contaminants during both phases of pilot-scale work at the WTC. The removal of conventional contaminants has been reported elsewhere (10-13).

EXPERIMENTAL PROTOCOL

Details of the pilot plant apparatus and operation have been extensively reported (10-13). The pilot plant was designed to operate as a two stage separate sludge pre-denitrification nitrification system to effect complete nitrogen control and the oxidation of phenolic compounds, thiocyanate and cyanide in separate anoxic and oxygenic biological fluidized bed reactors. Two phases of work were undertaken. In Phase 1, treatment of coke plant wastewater only was evaluated. Treatment of a mixture of coke plant wastewater and blast furnace blowdown water was studied in Phase 2.

The experimental approach followed was to determine those operating conditions required to maintain stable nitrification and complete denitrification. The performance of the total system was measured in terms of the change in effluent quality resulting from progressive increases in loading to the reactors. Sampling and analytical methods for conventional parameters are described in previous publications (14,15).

Coke plant wastewaters were obtained in both phases from the byproduct coke plant at Dofasco Inc. in Hamilton, Ontario. For the second phase of work, blast furnace blowdown water was obtained from a second integrated steel mill. Ratios of blast furnace blowdown water to coke plant wastewater of two to one and three to one (by volume) were used to simulate the anticipated range of operating conditions at Dofasco. Detailed characterization of both wastewaters has already been reported (10-13).

All aqueous and biological sludge samples (except for sludge samples from Phase 2) were extracted and analyzed by GC/MS protocol. Phase 2 sludges were analyzed by HPLC protocol. Table 1 summarizes the types and number of samples collected.

In Phase 1, grab samples of four batches of untreated coke plant wastewater that were used as feed to the fluidized bed system were manually collected on a non-routine basis. In Phase 2, seven batches of combined coke plant wastewater and blast furnace blowdown water were sampled. Analysis of the individual components of the combined feed was carried out on two occasions. Grab samples of fluidized bed effluent were taken after equilibrium conditions had been achieved. Five samples were taken during Phase 1. Also, the effluent was sampled three times during an unsteady-state portion of Phase 1 to define process performance under variable feed conditions (11). Seven effluent samples were taken during Phase 2.

TABLE 1. SAMPLE COLLECTION

Phase No.	Number of Samples Untreated Wastewater	Treated Effluent	Sludges
1	4	8	11
2	7	7	10

Excess biomass separated from the support medium in both fluidized beds was sampled on a non-routine basis. Eleven samples were taken during Phase 1, seven from the denitrification reactor and four from the nitrification reactor. Ten samples were taken during Phase 2, five from each fluidized bed reactor.

All samples were analyzed for trace organic contaminants by the WTC Laboratory Services Section using modifications of the U.S. EPA standard procedures for wastewater (16) and the U.S. EPA interim procedures for sludges (17,18). Samples were analyzed in duplicate to determine precision of measurement. Duplicates of samples were also spiked with known quantities of specific organic contaminants to generate recovery data used to compute accuracy of measurement.

RESULTS

OPERATING AND PERFORMANCE DATA

A summary of the operating and performance data for Phases 1 and 2 is presented in Table 2. A more complete analysis has been presented elsewhere (10-13).

QUALITY ASSURANCE/QUALITY CONTROL

Considerable variation in recovery data was observed in untreated wastewater samples. This was largely attributed to the presence of high concentrations of phenol. The analytical protocols used were suitable for trace quantities of organic contaminants. The presence of high concentrations of a specific organic contaminant such as phenol saturated the solvent used in the protocol and reduced its capacity for extracting those compounds which were present at much lower concentrations. Therefore, the concentrations reported for untreated wastewaters should be considered order of magnitude estimates of the actual concentrations present.

TABLE 2. SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE DATA.

Phase No.	Operating Conditions			
	HRT (h)		SRT (day)	
	DN[1]	N[2]	DN	N
1	1.9 - 9.8	14.0 - 35.0	5.6 - 320	52 - 140
2	0.5 - 2.6	3.5 - 17.5	13 - 47	72 - 650

	Performance Data[3]			
	FOC	Phenolics	NH_3N	CNS
1	52.6/90.6-95.1	0.14/>99.9	1.2/98.8-99.9	2.2/99.2-99.6
2	23.0/85.2-90.6	0.09/>99.9	1.4/95.9-99.2	0.7/99.2-99.7

[1] Denitrification reactor.
[2] Nitrification reactor.
[3] Performance data are expressed as median effluent data in $mg \cdot L^{-1}$/range of removals in per cent.

Tables 3 and 4 present recovery data from Phase 2 for untreated combined wastewater, treated effluent and sludges. Table 3 includes priority pollutant recovery data. Table 4 shows non-priority pollutant recovery data. Although there was significant variability in the spike recovery from compound to compound, recoveries were generally higher and more consistent for treated effluent samples than for untreated wastewater samples. Recovery of base/neutral priority pollutants was generally more consistent than recovery of acid priority pollutants in both cases. For organic non-priority pollutant compounds, recoveries were comparable to those achieved for base/neutral priority pollutants. Recovery of spiked compounds from sludge samples was generally lower than the recovery of similar compounds from aqueous samples.

Recovery of base/neutral organic priority pollutants from treated effluents (Table 3) were generally in the range 60 to 90 per cent. Recovery of 60 to 140 per cent of the base/neutral organic non-priority pollutants was attained (Table 4). Although the absolute values reported for treated effluent samples should be treated with caution, the order of magnitude reduction in concentration of trace organic contaminants after fluidized bed treatment is considered to be valid on the basis of these QA/QC data.

The trace organic contaminant data presented in this paper are not corrected for recovery data.

TRACE ORGANIC CONTAMINANTS IN UNTREATED WASTEWATERS

Concentration data for organic priority pollutants found consistently in untreated wastewaters that were used in both Phases 1 and 2 are compared in Table 5. Non-priority pollutant concentration data are similarly presented in Table 6. In general, lower levels of trace organic contaminants were observed in combined wastewater samples than those of coke plant wastewater alone.

Of the acid extractable priority pollutants, phenol and 2,4-dimethyl phenol were found in most samples from both Phases 1 and 2 but at levels significantly lower than those determined by the traditional 4-amino-antipyrine method. Similar differences have been reported by other researchers (5,19).

The base/neutral priority pollutants identified in untreated wastewater samples were consistent with other observations (1,4-6). In Phase 1, nine base/neutral priority pollutants were identified at greater than trace concentrations in more than one sample. Shown in Table 5 are those base/neutral priority pollutants with mean concentrations for all samples greater than the detection limit ($0.01\ mg \cdot L^{-1}$). Only di-n-butyl phthalate and 1,3-/1,4-dichlorobenzene were found in combined wastewater samples and they were found in both Phases 1 and 2.

TABLE 3. RECOVERY OF SPIKED PRIORITY POLLUTANTS IN PHASE 2.

Contaminant	Mean Recovery (Per Cent ∓ Std. Dev.)[1]		
	Untreated Combined Wastewater	Treated Effluent	Sludges
Acenaphthene	56.5[2]	–[3]	12.2 ∓ 10.7
Acenaphthylene	67.0	–[3]	8.8 ∓ 8.9
Anthracene	67.5	–[3]	26.2 ∓ 11.1
Phenanthrene	66.5	–[3]	27.6 ∓ 22.7
Benzo(a)anthracene and/or chrysene	32.0	–[3]	50.8 ∓ 19.1
Benzo(a)pyrene	39.0 ∓ 33.6	64.4 ∓ 35.4	33.7 ∓ 10.8
Fluoranthene	74.5	–[3]	36.0 ∓ 15.4
Fluorene	79.0	–[3]	23.8 ∓ 23.4
Naphthalene	43.0 ∓ 33.5	62.9 ∓ 32.5	6.9 ∓ 5.6
Pyrene	49.7 ∓ 24.2	65.1 ∓ 27.9	28.6 ∓ 12.9
Di-n-butyl phthalate	52.6 ∓ 43.8	85.0 ∓ 66.4	26.5
Phenol	952 ∓ 1020	11.7 ∓ 9.6	9.0

[1] Recovery was considered to be equal to zero (0 per cent) in samples where a spiked compound was not recovered. Spike levels were at 100 µg.

[2] Where no std. dev. is given, data are for mean of two determinations.

[3] Recovery data for these compounds were not evaluated for effluents.

TABLE 4. RECOVERY OF SPIKED NON-PRIORITY POLLUTANTS IN PHASE 2.

Contaminant	Mean Recovery (Per Cent ∓ Std. Dev.)[1]		
	Untreated Combined Wastewater	Treated Effluent	Sludges
Benzonitrile	57.3 ∓ 51.1	60.5 ∓ 5.5	3.0[2]
Isoquinoline	71.3 ∓ 124	91.7 ∓ 30.3	19.5
2-methyl naphthalene	81.3 ∓ 37.1	74.3 ∓ 7.6	15.5
Indole	75.3 ∓ 130	70.2 ∓ 10.6	28.5
7A-methyl quinoline	82.0 ∓ 21.7	76.0 ∓ 10.9	26.5
7B-methyl quinoline	79.0 ∓ 26.7	63.0 ∓ 34.4	12.5
3,4-and/or 5,6-benzoquinoline	63.0 ∓ 39.9	81.3 ∓ 15.5	42.0
Carbazole	17.3 ∓ 15.0	73.8 ∓ 14.1	38.5
2- and/or 8-methyl quinoline	63.0 ∓ 23.1	76.5 ∓ 8.0	22.5
Quinoline	172 ∓ 298	138 ∓ 139	23.0
1-methyl naphthalene	85.3 ∓ 33.5	103 ∓ 41.3	22.0
4-methyl quinoline	98.7 ∓ 32.3	84.2 ∓ 8.8	34.0
Dibenzofuran	76.7 ∓ 18.5	78.5 ∓ 9.1	15.5

[1] Recovery was considered to be equal to zero (0 per cent) in samples where a spiked compound was not recovered.

[2] Where no std. dev. is given, data are for mean of two determinations.

TABLE 5. TRACE ORGANIC PRIORITY POLLUTANTS IN UNTREATED WASTEWATERS

Contaminant	Mean Concentration ($mg \cdot L^{-1}$ ∓ Std. Dev.)	
	Phase 1 (Coke Plant Wastewater Only)	Phase 2 (Combined Wastewater)
Anthracene and/or Phenanthrene	0.08 ∓ 0.09	ND
Fluoranthene	0.02 ∓ 0.02	ND
Fluorene	0.01 ∓ 0.01	ND
Naphthalene	0.04 ∓ 0.03	T
Pyrene	0.02 ∓ 0.02	ND
1,3- and/or 1,4-dichlorobenzene	0.06 ∓ 0.10	0.03 ∓ 0.03
Di-n-butyl phthalate	0.04 ∓ 0.07	1.20 ∓ 1.40
Phenol[1]	61.42 ∓ 91.62	8.31 ∓ 7.40
2,4-dimethyl phenol	14.80 ∓ 24.75	0.07 ∓ 0.06

ND - Not detected in any sample.
T - Trace amounts (less than 0.01 $mg \cdot L^{-1}$) detected in more than one sample.
[1] - When analyzed by the 4-aminoantipyrene method, concentrations are for Phase 1--391∓176; for phase 2--119∓36 $mg \cdot L^{-1}$.

TABLE 6. TRACE ORGANIC NON-PRIORITY POLLUTANTS IN UNTREATED WASTEWATERS

Contaminant	Mean Concentration (mg$\cdot$L^{-1} ∓ Std. Dev.)	
	Phase 1 (Coke Plant Wastewater Only)	Phase 2 (Combined Wastewater)
Benzonitrile	ND	0.01 ∓ 0.01
Isoquinoline	2.33 ∓ 3.27	1.02 ∓ 1.33
2-methyl naphthalene	0.04 ∓ 0.05	ND
Indole	6.34 ∓ 10.25	6.65 ∓ 4.26
4-methyl quinoline	0.11 ∓ 0.11	0.11 ∓ 0.13
7A-methyl quinoline	0.54 ∓ 0.82	0.11 ∓ 0.08
7B-methyl quinoline	0.58 ∓ 1.06	ND
2,6- and/or 2,7-dimethyl quinoline	0.04 ∓ 0.03	ND
2,4-dimethyl quinoline	0.02 ∓ 0.03	ND
3,4- and/or 5,6-benzoquinoline	0.09 ∓ 0.07	ND
Carbazole	0.98 ∓ 0.92	0.52 ∓ 0.40
2- and/or 8-methyl quinoline	0.52 ∓ 0.82	0.15 ∓ 0.18
Quinoline	7.22 ∓ 5.89	5.56 ∓ 4.33
7,8-benzoquinoline	0.03 ∓ 0.04	0.02 ∓ 0.02
Aniline	0.11 ∓ 0.24	0.45 ∓ 0.52
Dibenzofuran	0.03 ∓ 0.04	ND

ND - Not detected in any sample.
T - Trace amounts (less than 0.01 mg$\cdot$L^{-1}) detected in more than one sample.

The apparent absence of other base/neutral priority pollutants in the combined wastewater samples could be attributed to the lower gross organic content (as measured by TOC) of the coke plant wastewater that was a part of the combined wastewater. Examination of two untreated coke plant wastewater samples from Phase 2 showed that the concentration of trace organic contaminants was significantly lower than was observed in Phase 1. Parallel analysis of two blast furnace blowdown water samples showed them to be relatively free of trace organic contaminants. Although a number of contaminants were identified, none were present at concentrations in excess of 0.02 $mg \cdot L^{-1}$.

Table 6 presents those base/neutral non-priority pollutants with mean concentrations for all samples greater than the detection limit. Isoquinoline, indole and quinoline were measured at mean concentrations greater than 1 $mg \cdot L^{-1}$ in both phases 1 and 2.

REMOVAL OF TRACE ORGANIC CONTAMINANTS

Mean concentrations of those priority and non-priority pollutants remaining in the treated effluent from the fluidized bed system are shown in Table 7. Other than the phenolics, di-n-butyl phthalate was the only priority pollutant consistently measured in the treated effluent at greater than the detection limit in both Phases 1 and 2. This phthalate ester was shown to be commonly present in coke plant wastewaters by the U.S. EPA (1). Phthalate esters are common plasticizers and the consistent presence of di-n-butyl phthalate at low levels in the raw and treated wastewater may indicate contamination of samples. Although care was taken during sample collection to prevent contact with plastic materials, many components of the pilot plant were plastic.

As was the case in untreated wastewaters, the concentration of phenolic contaminants was lower than that determined by wet chemical methods. The maximum single phenol concentration measured in treated effluent by the GC/MS procedure was 0.01 $mg \cdot L^{-1}$ compared to concentrations of phenolic compounds in the range from 0.05 to 0.20 $mg \cdot L^{-1}$ according to the 4-aminoantipyrine method.

7A-methyl quinoline was the only base/neutral non-priority pollutant consistently detected at greater than trace concentrations during Phase 1. There were no base/neutral non-priority pollutants consistently observed at greater than trace concentrations during Phase 2. The highest absolute determinations of those contaminants that occurred at trace concentrations in Phase 1 did not exceed 0.03 $mg \cdot L^{-1}$ despite reported influent concentrations in excess of 1 $mg \cdot L^{-1}$ (Table 6).

Although absolute comparison of influent and effluent concentrations is difficult owing to the problems encountered in analyzing the influent samples, it appears that the coupled biological fluidized bed process is

TABLE 7. TRACE ORGANIC CONTAMINANTS IN TREATED EFFLUENTS

Contaminant	Mean Concentration (mg•L^{-1} ∓ Std. Dev.)	
	Phase 1 (Coke Plant Wastewater Only)	Phase 2 (Combined Wastewater)
Priority Pollutants		
Acenaphthylene	T	ND
Anthracene or Phenanthrene	T	ND
Fluoranthene	T	ND
Pyrene	T	ND
1,3- and/or 1,4-dichlorobenzene	ND	T
Di-n-butyl phthalate	0.02 ∓ 0.03	0.12 ∓ 0.22
Di-ethyl phthalate	T	ND
Bis-(2-ethyl hexyl) phthalate	T	ND
Phenol[1]	T	ND
2,4-dimethyl phenol	T	ND
Non-Priority Pollutants		
Isoquinoline	T	ND
3,5-dimethyl pyridine	T	ND
Indole	T	ND
2- and/or 8-methyl quinoline	T	ND
4-methyl quinoline	T	ND
7A-methyl quinoline	0.01 ∓ 0.01	ND
2,6- and/or 2,7-dimethyl quinoline	T	ND
2,4-dimethyl quinoline	T	ND
3,4- and/or 5,6-benzoquinoline	T	ND
Carbazole	T	ND
Quinoline	T	ND
7,8-benzoquinoline	T	ND

ND - Not detected in any sample.
T - Trace amount (less than 0.01 mg•L^{-1}) detected in more than one sample.
[1] - When measured by the 4-aminoantipyrene method, concentrations are, for Phase 1--0.15∓0.04; for Phase 2--0.09∓0.04 mg•l^{-1}.

capable of effecting a high degree of trace organic contaminant control on the basis of order of magnitude differences between influent and effluent trace organic contaminant concentrations.

TRACE ORGANIC CONTAMINANTS IN SLUDGES

The accumulation of priority and non-priority organic pollutants in biological sludges is shown in Table 8. Data are included for sludges from both nitrification and denitrification reactors. Only four base/neutral priority pollutants were detected at greater than trace concentrations (0.2 $mg \cdot kg^{-1}$ on a dry weight basis) in more than one sample. Two were phthalate esters, di-n-butyl phthalate and bis-(2-ethylhexyl) phthalate, which accumulated in the sludges at concentrations in the range from 1 to 30 $mg \cdot kg^{-1}$. Bridle et al (6,9) reported similar concentrations in biomass from suspended growth reactors treating coke plant wastewater. Other base/neutral priority pollutants consistently identified in the sludges were acenaphthylene and pyrene, found at concentrations up to 2 $mg \cdot kg^{-1}$. The presence of pyrene was also reported by Bridle et al (6,9) at similar concentrations in suspended growth sludges. None of the base/neutral non-priority pollutants were consistently identified at greater than trace levels.

In Phase 2, three sludge samples from both reactors were analyzed by HPLC methodology for PAHs only. The results from these samples, shown in Table 9, suggested an accumulation of PAHs during Phase 2. However, there are insufficient data available to conclude that the increase in PAH concentration in the sludges was significant.

EFFLUENT DISCHARGE LIMITATIONS

To place in perspective the performance of the fluidized bed process, the effluent quality achieved in the pilot-scale system was compared to the BPT and BAT effluent limitation guidelines promulgated by the U.S. Environmental Protection Agency for the iron and steel manufacturing point source category (20). It has been shown in a previous publication (13) that it is more economical to treat coke plant wastewater and blast furnace blowdown water simultaneously through the fluidized bed system rather than via treatment systems designed specifically for each wastewater. For this reason, this comparison is based upon the pilot plant performance attained with the combined wastewater (Phase 2). For the purposes of this comparison, the effluent limitations for both categories of by-product coke-making and iron blast furnace operation were summed to provide the total discharge limitation for the combined operations shown in Table 10.

The calculated effluent limitation guidelines for the by-product coke plant were based on actual Dofasco coke oven production rates (3850 $kkg \cdot d^{-}$). A theoretical blast furnace production rate of 6030 $kkg \cdot d^{-1}$ was assumed. The discharge loadings from the fluidized bed system were based on the average concentration of trace organic contaminants achieved by the

TABLE 8. TRACE ORGANIC CONTAMINANTS IN SLUDGES FROM PHASE 1

Contaminant	Concentration ($mg \cdot kg^{-1}$)[7]	
	DN[1]	N[2]
Priority Pollutants		
Acenaphthylene	0.14 ∓ 0.30[3]	ND[5]
Anthracene/Phenanthrene	T[6]	T
Fluoranthene	T	T
Pyrene	0.56 ∓ 0.72[3]	T
Di-n-butyl phthalate	3.93 ∓ 5.63[3]	11.25 ∓ 15.80[4]
Di-ethyl phthalate	T	T
Di-methyl phthalate	T	ND
Bis-(2-ethyl hexyl) phthalate	0.19 ∓ 0.33[3]	4.1 ∓ 6.08[4]
Isophorone	T	T
Non-Priority Pollutants		
Indole	T	ND
Carbazole	T	ND
2,6-dimethyl pyridine	T	ND
7,8-benzoquinoline	T	ND
9H-anthracene carbonitrile	T	T

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[1] DN - Denitrification reactor.
[2] N - Nitrification reactor.
[3] Mean conc. ($mg \cdot kg^{-1}$ on dry weight basis) and std. dev. of 7 samples.
[4] Mean conc. ($mg \cdot kg^{-1}$ on dry weight basis) and std. dev. of 4 samples.
[5] ND - Not detected in any sample.
[6] T - Trace amounts (less than 0.2 $mg \cdot kg^{-1}$) in more than one sample.
[7] Analysis by GCMS.

TABLE 9. TRACE ORGANIC CONTAMINANTS IN SLUDGES FROM PHASE 2

Contaminant	Concentration (mg•kg^{-1})[1]					
	DN Reactor			N Reactor		
Anthracene	ND[2]	ND	ND	ND	ND	0.2
Phenanthrene	T[3]	ND	0.4	T	ND	0.7
Benzo(a)anthracene and/or chrysene	ND	T	3.3	T	1.9	5.8
Benzo(b) and/or benzo(k)fluoranthene	ND	ND	5.7	ND	1.8	1.0
Benzo-a-pyrene	2.0	ND	ND	ND	T	1.3
Fluoranthene	ND	1.2	ND	0.4	2.2	6.9
Naphthalene	T	T	0.2	T	T	T
Pyrene	3.0	0.7	5.0	2.0	2.3	6.1

[1] mg•kg^{-1} expressed on a dry weight basis. Analysis by HPLC.
[2] ND - Not detected.
[3] T - Trace amounts (less than 0.2 mg•kg^{-1}).

TABLE 10. COMPARISON OF FLUIDIZED BED EFFLUENT QUALITY WITH U.S. EPA BPT AND BAT EFFLUENT LIMITATIONS

Contaminant	Byproduct Coke Plant Limitations		Iron Blast Furnace Limitations		Total Discharge Limitations	Fluid Bed Effluent Discharge	
	kg•kkg^{-1}	kg•d^{-1}	kg•kkg^{-1}	kg•d^{-1}	kg•d^{-1}	mg•L^{-1}	kg•d^{-1}
BPT							
Ammonia-N	0.0912	351.1	0.0537	323.8	674.9	1.0	4.95
Phenolics[1]	0.00150	5.78	0.00210	12.7	18.5	0.085	0.42
Cyanide	0.0219	84.3	0.00782	47.2	131.5	0.75	3.71
TSS	0.131	504.4	0.0260	156.8	661.2	30.0	148.5
BAT							
Ammonia-N	0.0180	69.3	0.00292	17.6	86.9	1.0	4.95
Cyanide	0.00351	13.5	0.000292	1.76	15.3	0.75	3.71
Phenolics[1]	0.0000319	0.12	0.0000292	0.18	0.30	0.085	0.42
Naphthalene	0.0000064	0.025	--	--	0.025	0.0	0.0
Benzo(a)pyrene	0.0000128	0.049	--	--	0.049	0.0	0.0

[1] Phenolics analysis by 4-aminoantipyrene method.

pilot plant during the six month study on combined wastewaters. Total flow was assumed to be 4950 $m^3 \cdot d^{-1}$ based on actual Dofasco coke plant wastewater flows (1300 $m^3 \cdot d^{-1}$) and blast furnace blowdown rates equivalent to 2.8 times the coke plant wastewater flow (3650 $m^3 \cdot d^{-1}$). The selection of this ratio was discussed in an earlier paper (13).

On the basis of the foregoing assumptions, the fluidized bed treated effluent loadings in terms of the designated contaminants are compared with the BPT and BAT effluent limitation guidelines in Table 10. No analysis of volatile trace organic contaminants was undertaken in this study; hence, no comparison is offered for benzene. Neither naphthalene nor benzo(a)pyrene were detected in the samples of treated effluent collected during Phase 2 (Table 7). Data for effluent phenolics are taken from samples analyzed by the 4-aminoantipyrine method as required by the effluent limitation guidelines (20). Table 10 shows that BPT discharge limitations are readily met by the fluidized bed system. For BAT limitations, guidelines for naphthalene and benzo(a)pyrene are met but phenol limitations are exceeded by 40 per cent.

CONCLUSIONS

The coupled biological fluidized bed system was found to be an effective process for removing U.S. EPA acid and base/neutral organic priority pollutants as well as a range of base/neutral organic non-priority pollutants from coke plant wastewaters and blast furnace blowdown water:

- Nine U.S. EPA organic priority pollutants were identified at greater than trace concentrations in more than one sample of untreated coke plant wastewater. Of these, two acid extractable contaminants, phenol and 2,4-dimethyl phenol, and seven base/neutral contaminants were consistently found and their mean concentrations were greater than the detection limit of 0.01 $mg \cdot L^{-1}$.

- Blast furnace blowdown water was relatively free of trace organic contaminants.

- Only two acid extractable contaminants, phenol and dimethyl phenol, and two base/neutral contaminants, di-n-butyl phthalate and 1,3-/1,4-dichlorobenzene were consistently found in untreated combined wastewater samples.

- Fifteen base/neutral non-priority pollutants were identified at greater than trace levels in more than one untreated coke plant wastewater. Ten were identified in samples of untreated combined wastewater.

- Only di-n-butyl phthalate of the U.S. EPA priority pollutants was consistently found at greater than trace levels in effluent samples when treating coke plant wastewater with or without blast furnace blowdown water.

- Of the non-priority pollutants, only 7A-methyl quinoline was consistently detected at greater than trace levels during treatment of coke plant wastewater alone. No non-priority pollutants were consistently detected at greater than trace levels in samples of treated combined wastewater.

- Four base/neutral priority pollutants were identified at greater than trace concentrations in more than one sample of reactor sludge during treatment of coke plant wastewater alone. Two were phthalate esters and two were PAHs. The same phthalate esters were found when the system was treating combined wastewater.

- BPT effluent limitation guidelines were met for phenolics.

- BAT effluent limitation guidelines were met for naphthalene and benzo(a)pyrene. They were exceeded by 40 per cent for phenolics.

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BIOLOGICAL TREATMENT OF COKE PLANT WASTEWATERS
A THREE-YEAR OPERATING CASE HISTORY

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ABSTRACT

Armco operated a biological treatment facility at its Hamilton, Ohio, Coke Plant from March 1979 to May 1982. This facility was equipped with an integral clarification system and was designed to treat all wastewaters generated in the Coke Plant area simultaneously. These waste streams included the waste ammonia liquors generated by the battery flushing liquor system, waste generated in the "benzol yard" area by the crude light oil distillation system, and sanitary sewage. After pretreatment and equalization, the wastes were mixed and pumped to an extended aeration, activated sludge treatment system incorporating an integral clarification configuration.

During the operating life of the treatment facility, the system consistently removed phenol and thiocyanate and, except during certain upset episodes, was able to remove ammonia down to the current BAT concentration levels. This paper provides an analysis of the data collected during the three-year operating life of the facility and compares that data to the May 27, 1982, BAT effluent standards. The paper also contains a discussion of problems encountered with filamentous microorganisms, their effect on the system and steps taken to control the growth of the filamentous microorganisms and to eliminate the associated sludge bulking conditions.

The Hamilton Coke Plant, including the biological treatment facility, ceased operations in May 1982.

INTRODUCTION

Armco's Hamilton plant is located in New Miami, Ohio, on the Great Miami River. The plant historically produced metallurgical coke and coking by-products. Additionally, the plant produced coke gas and molten pig iron which was then transported to the Middletown plant, approximately 15 miles to the northeast. However, in May 1982 the Coke Plant, including the by-products facilities, ceased operations, thereby ending over eighty years of cokemaking in New Miami.

The Hamilton Coke Plant consisted of four Koppers-Becker underjet design batteries with a total of one hundred ten ovens. The oldest battery was constructed in 1928 and the newest battery in 1947. During the life of the batteries they were rebuilt several times with the latest rehabilitation taking place in 1977 and 1978.

A major part of the 1977-78 rehabilitation program for the Hamilton Coke Plant included the installation of state-of-the-art air and water pollution control facilities. The water pollution control program included the collection and treatment of sanitary sewage, ammonia still waste, benzol plant waste, quench tower waste, and high temperature noncontact cooling water. This paper deals with treatment of the sanitary sewage, ammonia still waste, and benzol plant waste. Specifically, the paper deals with the 38-month operation of the biological treatment plant and the problems associated with that operation. Additional details of the design and construction of this treatment plant and early performance data have been reported earlier.(1,2)

DESCRIPTION OF PRETREATMENT FACILITIES

The treatment plant process is shown schematically in Figure 1. As shown, the system received excess ammonia liquor generated in the flushing liquor system, benzol plant wastewater generated in the crude light oil distillation operations, and sanitary sewage from in-plant facilities. Each waste stream was pretreated before being discharged into the biological treatment process.

Excess ammonia liquor was pretreated in an ammonia distillation column to remove both free and fixed ammonia. The liquor was injected into the free leg of the ammonia still near the top of the still column. After passing through the free leg, the liquor was withdrawn from the column. Caustic soda was added to raise the pH and the mixture passed through a motionless mixer prior to injection into the fixed leg. Low pressure exhaust steam was injected at the base of the still and bubbled through the descending flow of liquor to strip the ammonia. The ammonia vapors and acid gases were collected at the top of the still, cooled to condense excess water and discharged into the coke gas line downstream from the primary cooler. The ammonia was later recovered from the gas as ammonium sulfate, a by-product.

The benzol plant waste contained large quantities of oil. To remove the free oil and to minimize the potential detrimental effect of large quantities of free oil on the biological treatment plant, the waste stream was treated in a gravity oil/water separator. After removal of the free oil the waste stream was mixed with the ammonia still waste stream and pumped to the biological treatment plant surge tank for equalization prior to treatment.

The combined "process waste" stream consisting of the excess ammonia liquor and the benzol plant wastes was received at the treatment plant in the process surge tank. This tank, which had a working volume of approximately 300,000 gallons, provided flow and chemical equalization of the waste. The tank normally operated at 50% full and thereby provided storage of the waste for approximately one day prior to treatment in the aeration system.

Following equalization, the process waste was still approximately 50°C to 70°C and required cooling prior to discharge to the bioplant. This cooling was achieved in two parallel spiral flow heat exchangers. To compensate for the hot blower air used in the aeration process, and other heat sources, the liquor was cooled to about 20°C during the summer months to maintain the desired operating temperature of 25°C in the aeration basins.

The biological treatment plant received the sanitary sewage in a central pumping station. From this point the waste stream was pumped through a comminutor to break up any large solids and discharged into an aerated sanitary surge tank for equalization. The equalized sanitary waste stream was then combined with the process wastewater and discharged into the aeration basin.

To maintain the nutritional balance of the aerobic system, phosphoric acid was added to the liquor just after it passed through the heat exchangers. At the same point, sulfuric acid was added for pH control when the pH of the basin exceeded the desired 7.8 operating point. Because caustic soda addition equip- ment was not provided, manual addition of soda ash directly into the aeration basins was necessary when the pH dropped below 7.0. Following chemical addition, the total flow was discharged into two parallel aeration/clarification basins.

DESCRIPTION OF BIOLOGICAL TREATMENT FACILITIES

The treatment system utilized a completely mixed, activated sludge extended aeration concept with an integral clarifier. The aeration portion of the plant contained two cubical concrete basins each with its own clarifier section. Each basin had one submerged turbine aerator to achieve complete mixing and oxygen transfer. Three rotary lobe positive displacement air blowers were used to generate the supply of air to the submerged turbine aerator. The aeration/ clarification configuration shown in Figure 2 allowed the aerator to develop a horizontal velocity along the surface of the aeration basin. This, in turn, caused a downward flow of approximately ten times the once-through flow in the "chimney" or the space provided between the aeration section and the clarification section. The majority of this flow passed back into the aeration basin, carrying with it the solids settled in the clarifier section. This action provided a theoretical recycle rate of 200%. The flow into the clarifier was equal to the incoming waste. This flow entered at the bottom along the length of the clarifier, passed vertically up through the clarification section, and finally discharged from the system. A scraper moved the settled sludge down the sloped clarifier bottom to the chimney area where it was resuspended and carried back to the aeration basin.

A treatment plant graphic control panel enabled the operator to monitor the physical operations of the plant including flows, temperatures, tank levels, etc., and to make minor corrections as required. The system continuously monitored the aeration dissolved oxygen, temperature and pH and automatically controlled the latter two. Based on these controls and chemical analysis made in the treatment plant laboratory, adjustments were made to the system.

DISCUSSION OF TREATMENT PLANT START-UP

In March 1979 the treatment system was started up using the north aeration/clarification basins only, due to start-up problems encountered with the south mixer. Additional construction delays were encountered in the ammonia still area and the benzol yard area which delayed the stripping of ammonia from the flushing liquor stream until July 1979 and delayed the treatment of the benzol waste stream until September 1979.

On March 14, 1979, an extremely dilute solution of feed stock at approximately 20 GPM was fed into the aeration basin which had been seeded with 3000 gallons of activated sludge from the Middletown, Ohio, POTW. During the following days, additional truckloads of sludge were pumped into the system until the mixed liquor was at 1200 mg/L MLTSS. Since the Middletown POTW treats wastewaters from Armco's Middletown Coke Plant, the microorganisms were acclimated to Coke Plant wastes and adapted to the new environment quite rapidly. By day thirty the mixed liquor had increased to 6,000 mg/L and continued to rise until it reached a high of 15,000 mg/L at day 185 (September 14, 1979) when the second aeration basin came on-line.

While operating with only one aeration basin the system consistently removed phenol and thiocyanate, but achieved little or no removal of ammonia even after the ammonia still came on-line. On day 71 (May 23, 1979), caustic soda was first utilized to enhance ammonia stripping, but because of additional start-up problems with the caustic soda feed pumps and pH control instrumentation at the ammonia still, the effect of the enhanced stripping was not evident at the bioplant until day 103 (June 24, 1979). From day 103 until day 217 (October 16, 1979), or 32 days after the start-up of a two basin operation, ammonia removal was erratic at best, and the system was difficult to operate. The plant would achieve nitrification thus depleting alkalinity in the system, thereby driving down the pH. Without caustic soda addition equipment at the bioplant the operators were unable to effectively control the pH of the system. When these severe drops in pH occurred the nitrification essentially stopped. After start of both basins ammonia removal was consistent and the system was more stable.

DISCUSSION OF OPERATING PROBLEMS

During the first fourteen months of operation of the biosystem the production at the Coke Plant was very stable with monthly production consistently around 1,250 tons per month. However, during month fifteen (May 1980) the Coke Plant severely curtailed production to a low of approximately 700 tons per month. As shown in Figure 3 the production was quite erratic for the remainder of the campaign. The effect of this curtailed production was to reduce the flows and pollutant loadings to the biosystem. Although the reduction in the production level created no apparent ill effects in the biosystem at the time, it started a trend which may have contributed to an upset which occurred in month 18 (August 1980).

Figure 4 shows the average monthly wastewater flows that were treated in the treatment system. The sharp increase in process waste and river water flows in month 7 (September 1979) was caused by the introduction of the benzol yard waste for the first time and the use of river water in a foam spray system. The foam spray system was installed because of severe foaming problems experienced during start-up while operating on one basin and associated problems with over-dosing anti-foam, thus affecting mass transfer efficiency. After the second aeration basin was started, the system stabilized causing the foam to subside and allowing decreased use of river water during early 1980 as shown in Figure 4, months 8 to 13. As shown in Figure 4, there was a marked decrease in process water starting with month 14 (April 1980) and continuing to a low of only 54,000 GPD of process water in August 1980 (month 18). This coincides exactly with the reduced production noted above.

Starting during month 10 (October 1979) and lasting thru month 17, the system was extremely stable and achieved remarkable removals of phenol, ammonia, thiocyanate, BOD_5, and COD. As shown in Figure 5 the biomass inventory in the system climbed steadily to month 17 (July 1980), when it contained over 70,000 pounds of biomass. At this time the basins achieved a peak mixed liquor concentration of 22,700 mg/L. Prior to month 18 the only hint of problems with holding a high mixed liquor system occurred in months 6 and 7 (August/September 1979) as shown by the high suspended solids in the effluent in Figure 6. This problem is attributed to a higher than typical flux rate to the clarifier. As shown in Figure 7, the peak flux rate in month 7 was nearly 90 pounds per day per square foot of clarifier surface as compared to the recommended maximum of 20 to 30 lbs/day/square foot.(3) Following the start-up of the two-basin operation in month 8, the flux rate dropped to 25 to 30 with a peak of 40 lbs/day/square foot and ran without difficulty until month 18.

During the first 17 months of operation, the apparent Sludge Volume Index (SVI) consistently ran in the range of 50 to 60. However, these apparently low values may have been misleading as they were calculated in strict accordance with procedures described in Standard Methods.(4) Standard Methods does not provide a procedure for SVI's in systems that are operating with high mixed liquor solids. If the mixed liquor suspended solids concentration is over 10,000 mg/L the Standard Methods formula creates a mathematical maximum value of 100 even if the sludge does not settle at all. Only after the cessation of operations did we discover that MOP/8(3) recommendss that "all SVI results should be determined at 2500 mg/L ± 500 mg/L," implying that all mixed liquor samples be diluted to that point. Standard Methods does not mention this procedure. Because of the reliance on the Standard Methods procedure and the potential misinterpretation of the data we may have missed indicators of problems to come.

On day 505 (July 30, 1980) the beginning of what later became a catastrophic loss of mixed liquor suspended solids occurred. On that day and on July 31, 1980, the operators first noted that excess solids were in the effluent of the north clarifier. On August 1, 1980, microscopic examination suggested the system was stressed. On day 510 (August 4, 1980), the system started consistently bulking and continued this trend thru October 1980. This is noted in Figure 5 with the extreme loss of inventory in months 18, 19, and 20. A corresponding increase in effluent suspended solids is noted in the same period in Figure 6. In August the operators' microscopic examination revealed that the biomass consisted mainly of filamentous organisms. A sample of the biomass was submitted to Armco's Environmental Research microbiologist for analysis. His report indicated that the filaments were Sphaerotilus natans, one of the most common forms of filamentous bacteria associated with sludge bulking.

A normal biomass system usually contains filamentous organisms in balance with the zooglea. In fact, the filaments provide a backbone for floc development resulting in a strong large floc.(5) It is when conditions favor the predominance of filaments that bulking problems occur. In this case they occurred quickly and with limited notice. MOP/8(3) and MOP/11(6) report several conditions which stimulate predomination of the filamentous bacteria over the normal floc-forming bacteria. These include, but are not limited to, such factors as low pH, an imbalance of nutrients, low dissolved oxygen, shock loadings, and high organic loadings. The Hamilton system experienced several of these and other conditions which may have contributed to the upset.

During the first 13 months of operation the temperature in the aeration basins averaged 25°C ± 1°, as is shown in Figure 8. However, in month 14 (on April 15, 1980) the heat exchangers began to foul with a calcium carbonate film on the process liquor side of the exchanger. This prevented effective cooling of the process waste and the aeration basin mixed liquor temperature rose to an average monthly temperature of over 32°C in months 17 and 18 (July/August, 1980). For four months the system operated at the elevated temperatures with no apparent ill effects and during this time continued to achieve excellent nitrification. Although we have found no literature reports correlating higher temperatures with the growth of filamentous bacteria, we believe that the high temperature may have contributed to the bulking problem. Jones, et. al.(7) recently reported the development of filamentous organisms starting day 52 and dominating by day

80 in a bench scale reactor treating high strength Coke Plant wastewater operated at 35°C. Wong-Chong(8) reports no occurrence of bulking due to filamentous organisms in equivalent systems operated at 20-25°C. The Hamilton treatment plant operated at temperatures in excess of 30°C for over 110 days before the domination of the filamentous bacteria occurred.

The condition which probably contributed most to the filamentous bacteria domination was an imbalance of nutrients. As shown in Figure 9 the ratio of COD to ammonia-nitrogen took a big jump in month 16 (June 1980) with only minimal improvement in month 17 (July 1980). MOP/8(3) suggests a BOD_5:ammonia-nitrogen: phosphorus ratio of 100:5:1 for municipal systems treating substantial industrial contributions or a COD/NH_3-N ratio of 20:1. Figure 9 suggests that the ammonia concentration should have been much higher since the ratio of COD to NH_3-N was nearly 60 in month 16 and over 40 in month 17. However, if other sources of nitrogen are considered, such as thiocyanate-nitrogen, the ratio is in the range of (10 to 15):1. Therefore, the more important factor may be the phosphorus concentration. During the last half of July 1980 (month 17), the phosphate concentration was very low in the biosystem resulting in a COD:P ratio of over 800 as compared to the MOP/8(3) suggested ratio of 100:1. Additionally, the plant had previously experienced an upset that was directly attributed to phosphorus deficiency when the phosphate level was inadvertently depleted.(1,2)

Another commonly suggested cause of filamentous domination is low dissolved oxygen in the mixed liquor system. A review of Figure 10 reveals no apparent problems as the daily average dissolved oxygen stayed well above 1.0 mg/L with the monthly average dissolved oxygen staying well above 3.00 mg/L. However, numerous short-term power outages occurred during the waning days of month 17 (July 1980) and early in month 18. These outages caused short-term depressions in the D.O. and, although they had no apparent effect on the system, they may have contributed to the long-term problems.

Figure 11 shows the minimum and maximum monthly pH values of the aeration basins. Even though the pH in Figure 11 varies from 6.6 to 8.3, the system was generally quite stable with the operators able to control the pH with acid additions or periodic additions of soda ash. During the period from month 15 to 18 the system was very stable with pH fluctuations of only ± 0.25 standard units and, therefore, pH fluctuations do not appear to have contributed to the upset.

Another area that must be noted as potentially contributing to the upset is the extremely low food to mass ratios leading up to day 510. As shown in Figure 12 the food to mass ratio, based on BOD_5, reached an average monthly low of 0.025 pounds BOD_5/pound MLTSS in month 15 and was only 0.03 in month 18 just before the upset. An all-time low of 0.019 pound BOD_5/pound MLTSS was observed in the days preceding the upset. This is far below the value normally considered to be optimum in municipal plants (MOP/11(6)) of 0.1 to 0.5 pound BOD_5/pound MLTSS and well below the long-term average of 0.08 pound BOD_5/pound MLTSS observed in the Hamilton plant. Additionally, the F:M ratios for COD phenol and ammonia were at an all-time low value prior to the upset. Because of the high surface-to-volume ratio of filamentous bacteria, and because the filaments projected from the floc into the substrate liquid, they have a competitive advantage. Figure 13 shows that the oxygen uptake was at its lowest in months 17 and 18, thus indicating a very inactive biomass. This is typical of a high mixed liquor system with long sludge ages and low F:M ratios.

In addition to the above stated operating condition, the system was operating with its longest ever Hydraulic Residence Times (HRT) and Theoretical Solids Residence Times (T-SRT). Figure 14 shows the HRT throughout the life of the plant. As shown, the system was operating with an HRT of over 55-60 hours in months 17 and 18 at the onset of the upset. The Theoretical SRT is not known as no accurate records of sludge wastage were kept. However, based on effluent solids and an estimate of wasted sludge, the T-SRT was several hundred days and is shown in Figure 15.

Although a shock load was suspected to have contributed to the upset, no specific parameter was identified. The only apparent shock load was a doubling of the phenol concentration in the process waste stream from 500 mg/L up to 1000 mg/L and an associated low ammonia concentration on day 510, the first apparent day of the upset. In addition, the COD in the influent increased from a normal of 2,000-3,000 mg/L to 4,800 mg/L on day 509.

DISCUSSION OF CORRECTION MEASURES

Several steps were taken to correct the upset caused by excess filamentous bacteria. The first step was to identify problems associated with the bulking sludge and to control the extreme loss of solids over the effluent weir. As noted above, samples were submitted to Armco Research who confirmed the operators' microscopic analysis as a filamentous-bacteria-associated bulking problem and identified the bacteria as Sphaerotilus natans. In an attempt to control the loss of solids the wasting of sludge was increased to the maximum possible. However, since the method of wasting was to return the sludge to the by-products operations, the amount of sludge that could be wasted was limited by the capacity of the flushing liquor system. Also, phosphate feeding was increased in an attempt to balance the nutrient requirements. Polymers were then added in an attempt to enhance settling, but yielded no improvements and appeared to aggravate a severe foaming problem that surfaced on day 526 (August 20, 1980). The polymer trial was then discontinued.

Following the initial steps, in an effort to minimize solids loss, the basin mixers were run intermittently starting on day 538 (September 1, 1980). By day 540, the clarifiers were inverted, apparently due to lack of sludge recirculation (as shown in Figure 2 the system relies on the pumping action of the mixers for sludge recirculation), and the associated anoxic condition of the clarifier. The floating solids were then pumped back into the aeration basin.

Following the recommendations made in MOP/11(6), an attempt was made to control the filaments using hydrogen peroxide (H_2O_2) as a disinfectant. Following various vendor recommendations and dosages suggested by bench scale test, 175 lbs/day of 100% H_2O_2 was added directly to the north aeration basin from day 552 (September 15, 1980) until day 556. The south basin was used as a control. A second test of 250 lbs/day of H_2O_2 was added to the north basin from day 577 (October 10, 1980) to day 586. Neither test showed any promise of breaking up the filaments and the practice was discontinued. At this point, the mixed liquor had dropped from a high of over 20,000 mg/L to the 600-700 mg/L range. Also, starting on day 577 calcium hypochlorite was added to the sanitary surge tank when filaments were discovered in that source. It was believed that the basin samples which were emptied into the sanitary sewer caused this problem.

At this point the operators felt that there were mechanical problems with the clarifier system and therefore emptied the north basins for inspection on day 587. The inspection revealed no mechanical anomalies, but because of the increased loading to the south basin may have contributed to the stabilization of the system. Starting on day 587 the mixed liquor concentration in the south basin began to increase and seemed to stabilize at about 4000 mg/L MLTSS.

In November 1980 (month 21), samples of the aeration basin foam were submitted to Armco Research for analysis and their recommendation for control. Research indicated the foam contained the bacteria Nocardia, a notorious foamer, in addition to the previously identified Sphaerotilus. The recommended procedure(5) to control Nocardia was to spray a 5% solution of sodium hypochlorite directly onto the foam. In early December 1980 (month 22) several gallons of 5% sodium hypochlorite were sprayed onto the foam. By the end of the first week of this practice, the Nocardia were under control.

On February 6, 1981 (day 696), the north basin was put back on-line and the two aeration/clarification basins ran in parallel for the remainder of the campaign. At this point the system had stabilized and ran smoothly until month 33. The operators never eliminated the filaments, but with careful control of the basin temperature and proper control of phosphorus and ammonia the system was quite stable. The mixed liquor did not attain the growth rate it had achieved before the upset, but it did gradually recover and stabilize at around 10,000 to 12,000 mg/L MLTSS.

Starting on day 983 (November 20, 1981), a series of oil spills occurred, allowing oil to be pumped into the aeration system. A second spill occurred on day 993 (November 30, 1981). A third occurred on day 1045 (January 21, 1982). These oil spills created problems resulting in excessive solids loss from the system. This is depicted in Figure 6 which shows high effluent suspended solids in months 33, 34, and 35. However, the system appeared to recover rapidly from these oil spills and they caused no long-term problems.

DISCUSSION OF OPERATING DATA

Table I and Table II show a comparison of the design and actual treatment plant flows and combined influent composition. As indicated on Table I, actual three year average flows were slightly lower than design except for the sanitary waste. This was caused by numerous occurrences of high flows from an unexplained source in the sanitary system. As shown on Table II, the loadings to the system were quite close to those expected during the design of the system. Table III shows select design criteria and a comparison to that actually experienced in the three year average. Table IV shows the concentration of various parameters in the concentrated process wastewater stream.

Figure 6 shows the effluent suspended solids achieved by the system over the 38 month campaign. As indicated, the system generally achieved an average monthly TSS level of less than 40 mg/L during the stable operation before the onset of the filamentous bacteria. However, the monthly average TSS level achieved by the system was more in the range of 80 to 100 mg/L with a three year average including the upsets of 140 mg/L.

As shown in Figure 16, the process waste stream influent phenol concentration varied from a monthly average of 200 mg/L to 1000 mg/L. The highest phenol concentration seems to coincide with the lowest production during month 18. Also shown in Figure 16 is the effluent phenol concentration. Except during start-up, the monthly average concentration generally was below 0.05 mg/L. The highest monthly averages occurred just after the filamentous bacteria upset. However, removals were excellent even during the time with minimal biomass inventory. As shown on Table V the three year average effluent phenol concentration was 0.023 mg/L.

Figure 17 shows the monthly average concentration of thiocyanate in the process waste stream and the average monthly thiocyanate concentration in the bioplant effluent. As indicated, the monthly average effluent concentration was generally less than 5 mg/L except during the upset period. During that time the average was generally around 10 mg/L and as shown on Table V, the three year effluent concentration was 7.0 mg/L including the early data during start-up. Excluding the early data the three year average effluent thiocyanate was 3.0 mg/L.

Figure 18 shows the monthly average process waste ammonia-nitrogen influent concentration and the monthly average effluent concentration for the 38 months of operation. The effluent ammonia was generally below 25 mg/L except during the several upsets experienced during the life of the system. Prior to month 7 the system was not achieving nitrification. From months 7 to 18 the system achieved excellent ammonia removal even in the first month of the filamentous upset. The high effluent levels of months 19, 20, and 21 were all caused by the filamentous bulking problem described above. The high effluent levels in month 25 (March 1981) were caused by the plugging of the ammonia still and the resultant high bioplant influent ammonia levels. The upset in month 32 (October 1981) is unexplained except for possible contamination of the caustic soda system with sodium aluminate. On day 945 (October 13, 1981), nitrification ceased for no apparent reason with an accompanying rise in pH and a resultant loss of mixed liquor solids. The operators suspected that the sodium aluminate that reached the bioplant may have precipitated the phosphate thus rendering it unavailable to the biomass. To compensate for the suspected precipitation of phosphate the phosphoric acid feed was increased. This appeared to work as nitrification resumed on day 954 (October 22, 1981). As shown on Table V, the long-term average of effluent ammonia excluding the early months of data was 20 mg/L.

Figure 19 shows the average monthly concentrations of cyanide in the process wastewater and the bioplant effluent. As shown, the cyanide varied from a low of 0.03 mg/L to a high of 70 mg/L in the process waste stream. The apparent rise in the process waste cyanide concentration in month 20 is unexplained.

COMPARISON OF EFFLUENT TO BAT STANDARDS

When the Hamilton biological treatment plant was constructed it was required to meet "effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available" (BPCTCA)(BPT).(10) These standards were much less restrictive than the May 27, 1982, "effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable" (BATEA)(BAT).(10) As such, there was no attempt made to control the plant to meet the BAT standards. However, because the plant did, in fact, achieve excellent results in terms of effluent quality, a comparison has been made to determine whether the plant achieved the BAT limitations. To make this comparison the actual average monthly discharge of a given parameter in pounds per day was divided by the actual production in that given month to obtain an actual discharge for a given month in terms of pounds discharged per one thousand pounds of coke produced. This was then compared to the BAT limitation(10) in pounds per thousand pounds and presented graphically in Figures 20 thru 24.

As Figure 20 shows, the average monthly flow rate from the biosystem exceeded the U.S.EPA base flow rate of 153 GPT ten times during the 38 month period. Figure 21 shows that the biosystem complied with the "best conventional technology" (BCT) average monthly limitation for total suspended solids of 0.14 lbs/1000 lbs in all but five of the 38 months. Additionally, Figure 21 shows ten months with exceedances of the maximum daily TSS limitation of 0.27 lb/1000 lbs. Figure 22 shows compliance with the "BAT" average monthly limitation of 0.0000319 lbs/1000 lbs for phenol in all but two of the 38 months, and eight exceedances of the maximum daily BAT limitation of 0.0000638 lbs/1000 lbs. Figure 23 shows that after month 7 (month nitrification achieved) the system complied with the BAT average monthly ammonia limitation of 0.016 lbs/1000 lbs in all except five of the 38 months and six months with exceedances of the BAT maximum daily ammonia limitation of 0.0543 lbs/1000 lbs. Figure 24 shows that there were six months that exceeded the BAT average monthly limitation for cyanide of 0.00351 lbs/1000 lbs and nine months with values that exceeded the BAT maximum daily cyanide limitation of 0.00638 lbs/1000 lbs.

CONCLUSIONS

The treatment of Coke Plant waste liquors to achieve phenol, ammonia, and cyanide removal in a single stage reactor proved to be a viable treatment method, although expensive when used in series with a caustic soda ammonia still. A single stage system is capable of achieving the U.S.EPA BAT limitations when well operated with particular attention to control of such factors as pH, temperature, ammonia-nitrogen, phosphorus, and other factors such as food to mass ratios and sludge age. Control of pH proved to be the most difficult factor because of the formation of acid in the treatment process and the destruction of the available alkalinity. The manual batch addition of bagged soda ash directly to the aeration basin as practiced at Hamilton is unacceptable and the authors suggest the addition of caustic soda or soda ash feeding equipment to any future bioplants. Also, control of the mixed liquor based on F:M ratios or sludge ages is essential. The installation of sludge disposal and, if necessary, dewatering equipment on-site is essential to control this parameter.

Operating the system with extremely high mixed liquors and long sludge ages in the aeration basin should not be a problem unless the domination of filamentous bacteria occurs. To prevent the domination of filamentous bacteria the authors suggest strict control of the above factors. Other than problems associated with filamentous, the system handled the high mixed liquor without problems during normal operations except for the one occurrence during start-up which was attributed to an excessive flux rate. When operating a system with high mixed liquor concentrations the authors suggest that a modified SVI per MOP/8 be used to monitor the system.

Negative effects on nitrification or phenol removal by the introduction of emulsified oil was never a problem. Emulsified oil in the effluent averaged less than 5 mg/L with an average inlet loading of over 40 mg/L. However, numerous upsets were caused by the introduction of free oil into the system. Therefore, it is essential that free oil from the by-products yard be completely removed before pumping liquor to the aeration system. Even with the best operated system with strict attention given to the operating parameters, upsets can occur. For example, the upset on day 945 was caused by no apparent reason other than a possible truck driver error. In this case sodium aluminate was pumped into the sodium hydroxide tank. If events such as this take place, or other operating errors are made in the by-products plant, upsets at the bioplant could occur, over which the bioplant operator has no control.

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TABLE I
BIOLOGICAL TREATMENT PLANT FLOWS

	Design Basis	Three Year Average
Total Process Waste	118,600	90,000
Sanitary Waste	21,800	28,900
River Water-Dilution	73,800	33,200
Total Effluent	214,200	152,100

TABLE II
COMBINED INFLUENT COMPOSITION

	Design Composition		Three Year Average	
	mg/L	#/Day	mg/L	#/Day
Ammonia-N	80	150	180	140
Cyanide	5	8	14	16
Thiocyanate	400	700	245	300
Phenol	250	440	240	300
COD	1800	3300	1950	2400
BOD	--	--	1300	1600

TABLE III
DESIGN CRITERIA

	Design	Actual Three Year Avg.
Detention Time - Total Flow	30 Hours	38 Hours
Clarifier Overflow Rate - Total Flow	300 GPD/SF	265 GPD/SF
Flux Rate	--	20 Lbs/Day/SF
Solids Retention Time	--	800 Days

TABLE IV
PROCESS WASTE INFLUENT COMPOSITION

	Design Composition	Three Year Average
	mg/L	mg/L
Ammonia-N	120	350
Cyanide	7	19
Thiocyanate	600	400
Phenol	380	420

TABLE V
BIOLOGICAL TREATMENT PLANT EFFLUENT

	Design Composition		Three Year Average	
	mg/L	#/Day	mg/L	#/Day
Flow (Total)	214,200 GPD		152,100 GPD	
Flow Rate (Total)	--			140 Gal/Ton
Ammonia-N	180	316	20	24
Cyanide	4.5	8	4.8	5.7
Thiocyanate	--	--	7.0	9.0
Phenol	3.0	5	0.023	0.028
Suspended Solids	70	130	140	150
COD	--	--		
BOD	--	--		

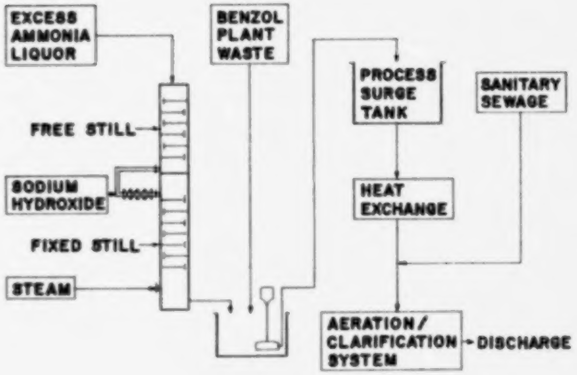
EXCESS AMMONIA LIQUOR
FREE STILL
SODIUM HYDROXIDE
FIXED STILL
STEAM
BENZOL PLANT WASTE
PROCESS SURGE TANK
HEAT EXCHANGE
SANITARY SEWAGE
AERATION / CLARIFICATION SYSTEM
DISCHARGE

FIGURE 1 SCHEMATIC OF TREATMENT PROCESS

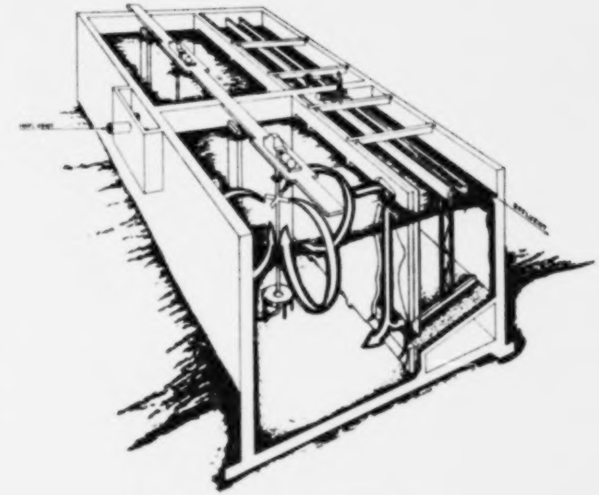

FIGURE 2 Schematic of Aeration / Clarification System

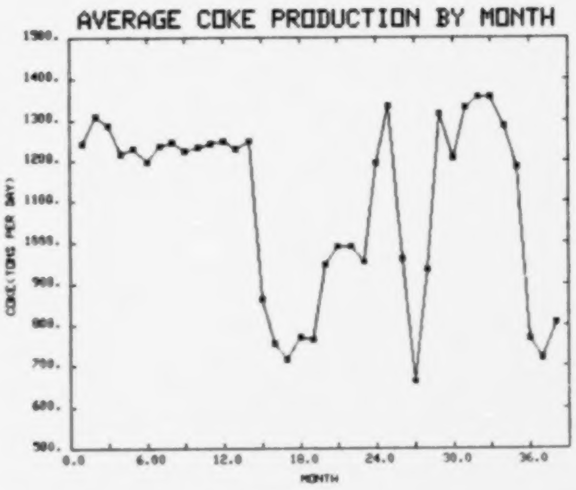

FIGURE 3

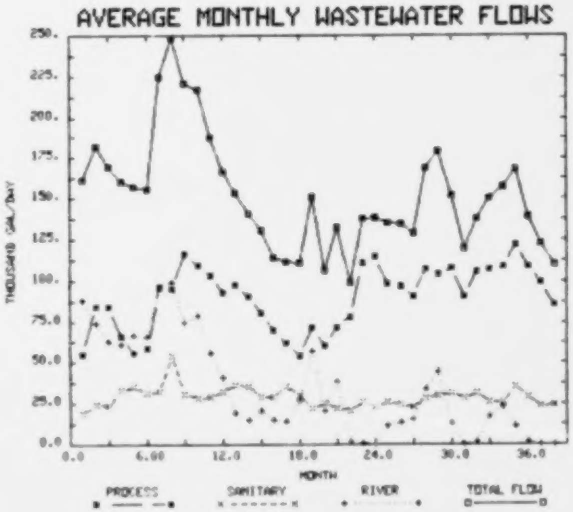

FIGURE 4

TOTAL BIOMASS INVENTORY-POUNDS MLTSS

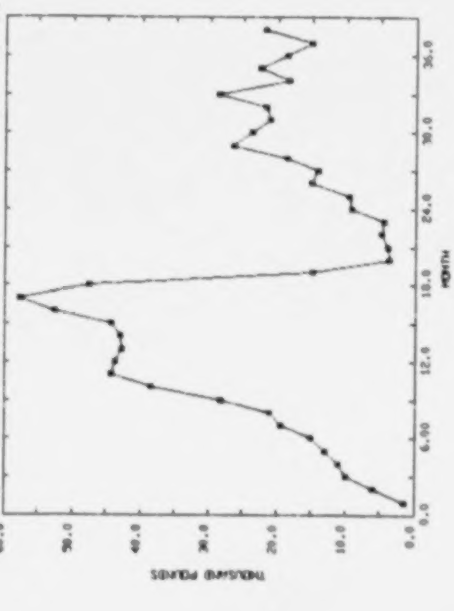

FIGURE 5

EFFLUENT SUSPENDED SOLIDS: MG/L

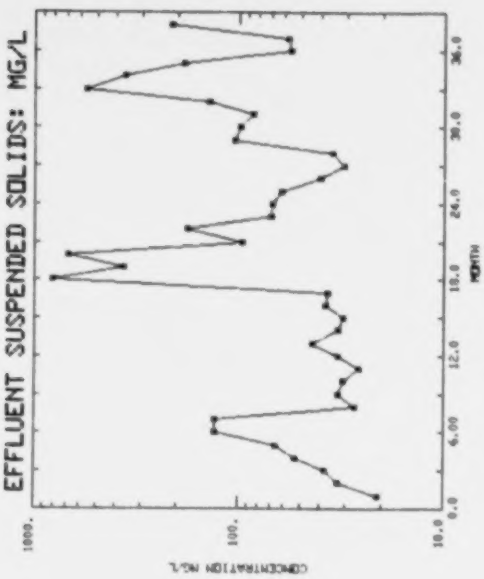

FIGURE 6

FLUX RATE TO CLARIFIER

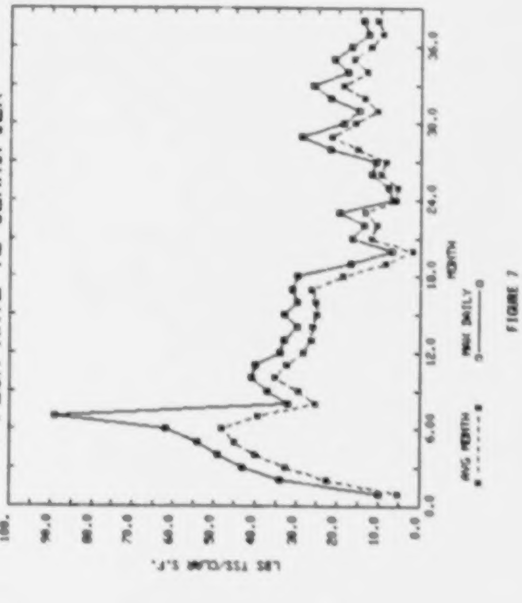

FIGURE 7

AERATION BASIN TEMPERATURE

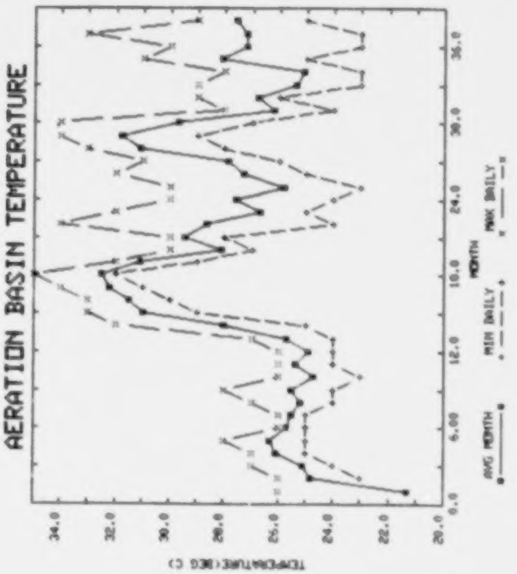

FIGURE 8

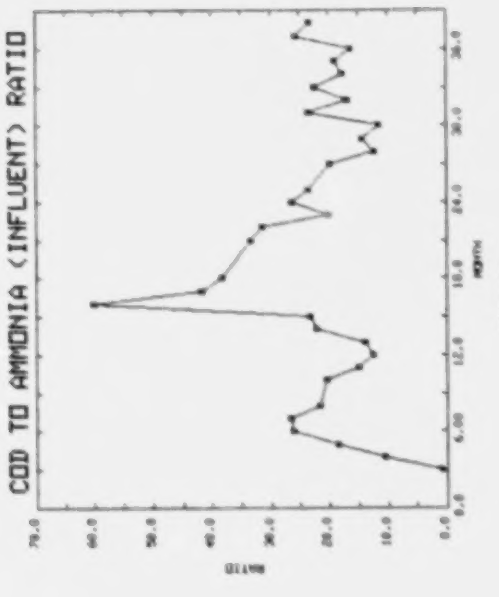

FIGURE 9

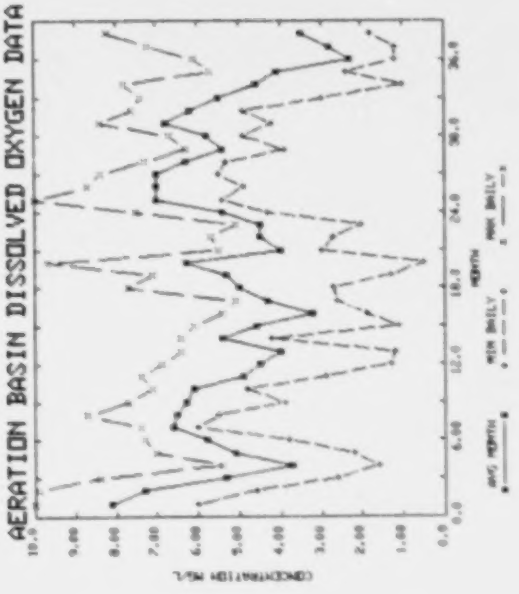

FIGURE 10

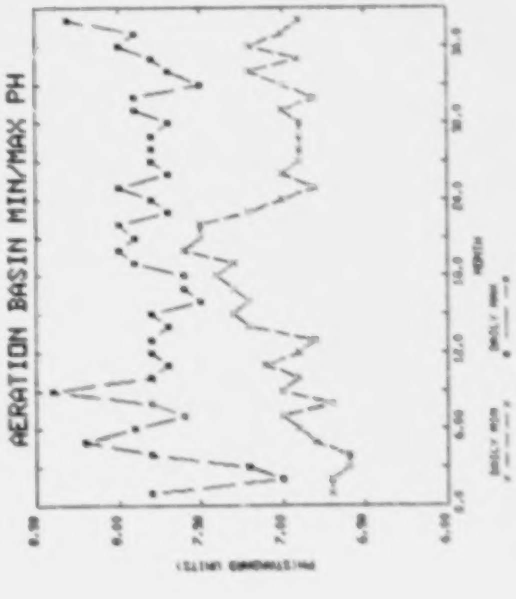

FIGURE 11

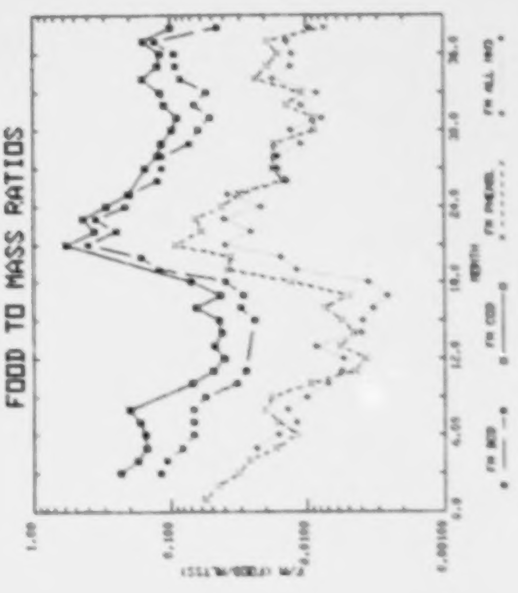

FIGURE 12

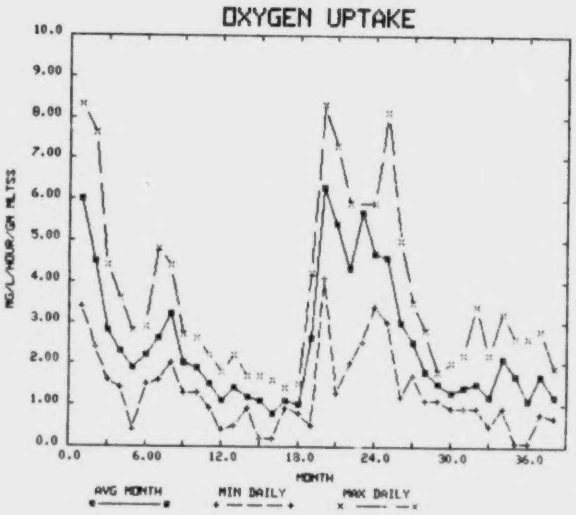

FIGURE 13

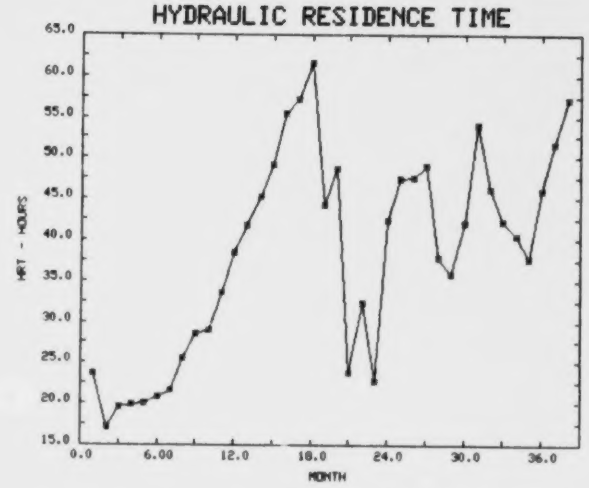

FIGURE 14

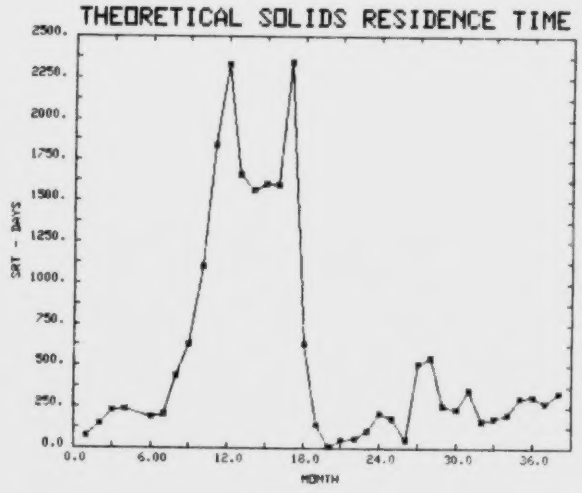

FIGURE 15

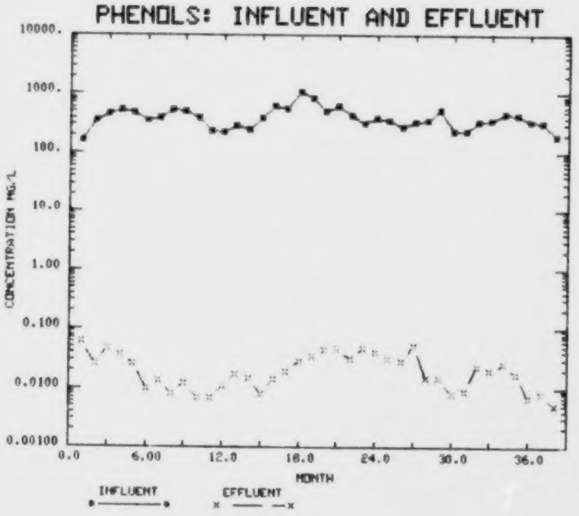

FIGURE 16

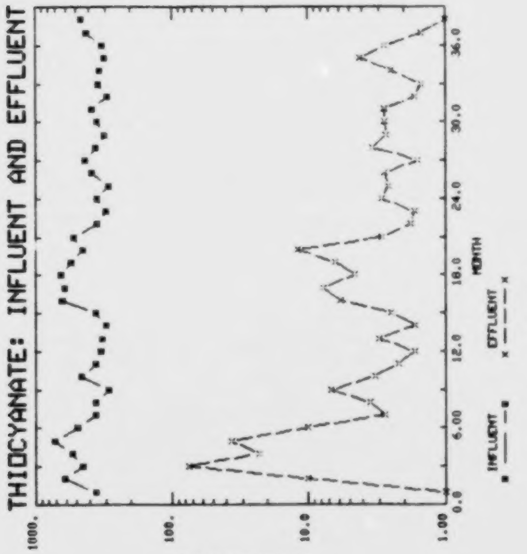

FIGURE 17

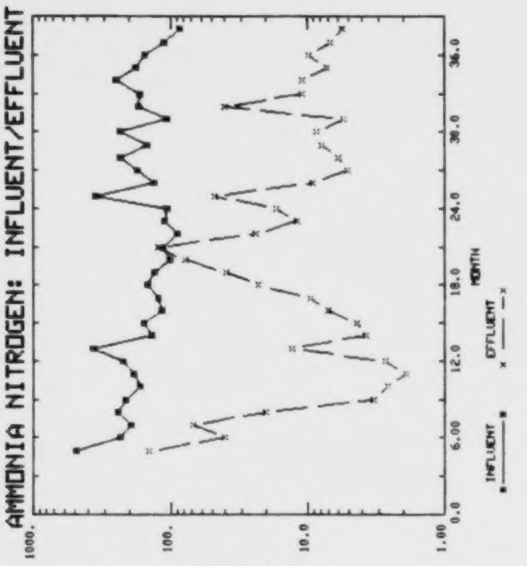

FIGURE 18

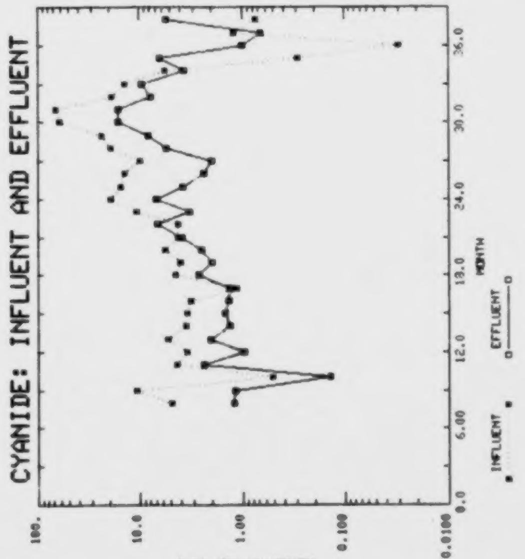

FIGURE 19

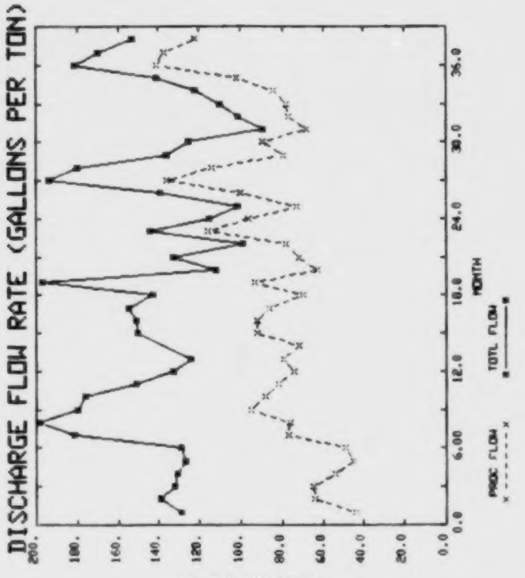

FIGURE 20

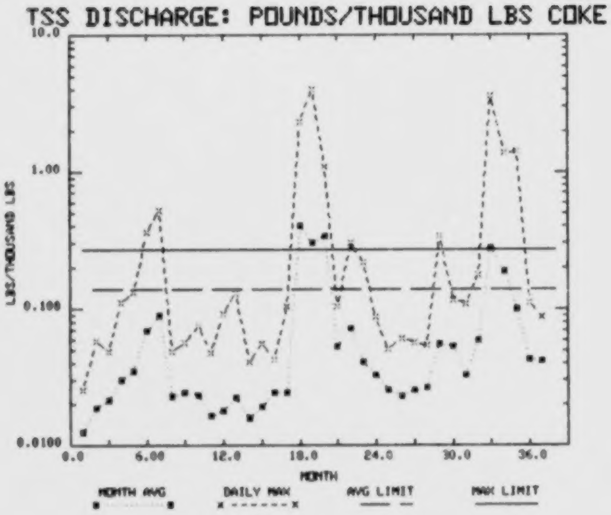

FIGURE 21

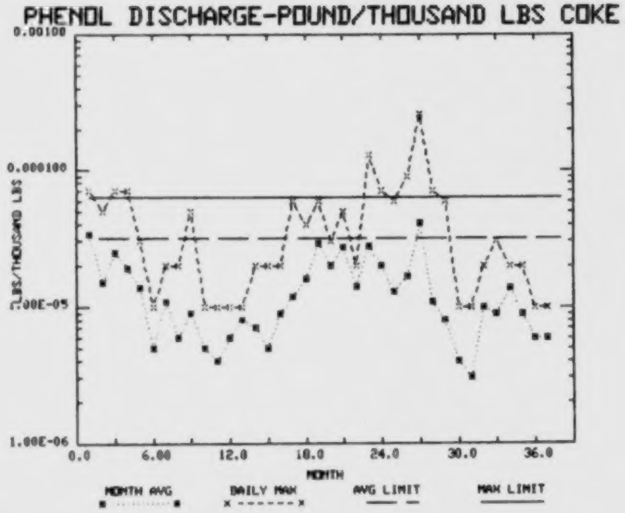

FIGURE 22

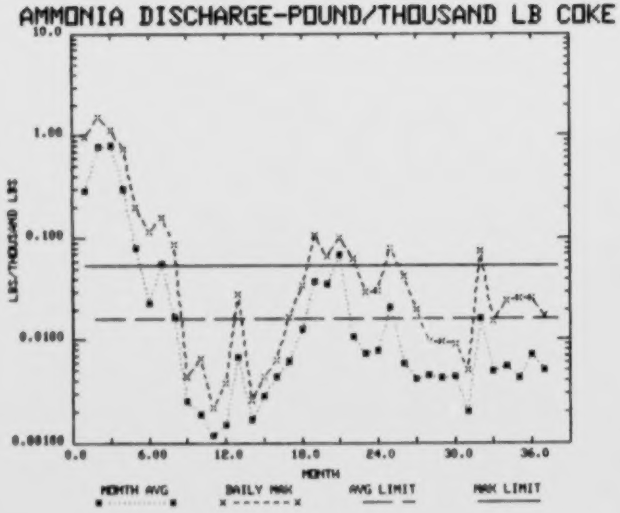

FIGURE 23

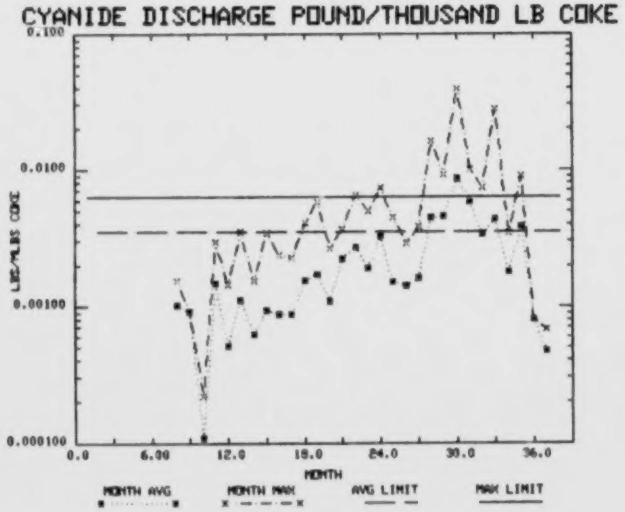

FIGURE 24

Ammonia and Hydrogen Cyanide Formation in Blast-Furnace Stack

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Ammonia and Hydrogen Cyanide Formation in Blast-Furnace Stack

by

E. T. Turkdogan and P. H. Josephic*

Abstract

The results of the present experimental study have substantiated the view that the volatile alkali cyanides carried by the furnace gas to the blast-furnace stack are responsible for the generation of ammonia and hydrogen cyanide in the upper part of the stack. Experiments were made under conditions similar to those in the upper part of the blast-furnace stack. In accord with the theoretical predictions, the experiments have shown that the reaction of water vapor with potassium cyanide, which is always vapor deposited on the burden in the stack, generates ammonia, which in turn reacts with carbon monoxide to generate hydrogen cyanide. Although oxidizing to ammonia, hematite and magnetite did not suppress ammonia generation. Also, small additions of manganese ore to the simulated blast-furnace burden did not suppress the generation of these volatile compounds.

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Introduction

The wash water for the blast-furnace off-gas invariably contains some ammonia, cyanides and phenols, in decreasing order. The enactment of legislations by federal and local governments have strictly limited the quantity of these contaminants that may be discharged to public waterways. Consequently, the efforts have been intensified in blast-furnace plants during the past decade to monitor the contaminants in the wash water and the variation thereof with the operation of the blast furnace, and to develop economical methods of decontaminating the wash water. For background technical information on the subject, selected publications are cited in References 1 to 8.

The contaminants in the wash water for the iron blast-furnace off-gas are in the ranges 10 to 300 mg NH_3/ℓ, 1 to 30 mg CN_t (total)/ℓ and 0.3 to 15 mg phenols/ℓ. In terms of ppm by volume in the stack gas, the concentrations are usually in the ranges 3000 to 4000 ppm NH_3 and 150 to 250 ppm CN_t. As observed by Pociecha and Biczysko,1) for example, most of the cyanide in the de-dusted furnace off-gas is in the form of hydrogen cyanide. They also found that the blast-furnace dust contains only a small amount of solid cyanides (presumably alkali cyanides) in comparison to the amount of hydrogen cyanide present in the de-dusted top gas. The same contaminants in the ferromanganese-blast furnace off-gas are about an order of magnitude greater than those in the iron-blast furnace.

Although the presence of ammonia and volatile cyanides in the de-dusted furnace off-gas, hence in the wash water, has been known for a long time, no study seems to have been made of the reactions that are responsible for the formation of these organic species in the blast-furnace stack. To study this phenomenon experimentally, let us first deliberate on the thermodynamics of some gas-gas and gas-solid reactions that are likely to occur in the blast furnace.

Theoretical Considerations

Unless stated otherwise, JANAF Thermochemical Tables[9)] are used in the calculations of reaction equilibria. Typical gas concentration ratios H_2/H_2O and CO/CO_2 in the blast-furnace stack vary with temperature as shown in Figure 1. The top gas temperature is at about 200°C and the gas ratios H_2/H_2O and CO/CO_2 are close to 1. For the temperature range 800 to 900°C the curve for CO/CO_2 is that for equilibrium with coexistent iron and wustite, as known to be the case in the stack. It is also known from the composition of gas samples, taken from various positions in the stack in many plant tests, that the water-gas shift equilibrium

$$\begin{gathered} CO + H_2O = CO_2 + H_2 \\ k = \frac{p_{H_2}}{p_{H_2O}} \; \frac{p_{CO_2}}{p_{CO}} \end{gathered} \tag{1}$$

prevails at temperatures above 700°C. The curve for H_2/H_2O in Figure 1 above 700°C is that calculated from the CO/CO_2 curve for reaction (1). An average value of P = 2 bar is taken for the total gas pressure in the stack with

$$\%CO + \%CO_2 = 42$$

$$\%H_2 + \%H_2O = 8$$

$$\%N_2 = 50$$

In the furnace hearth and combustion zone the gas composition is taken as 35 percent CO, 8 percent H_2 and 57 percent N_2 with total pressure P = 4 bar.

Calculated equilibrium concentrations of species hydrogen cyanide, HCN, isocyanic acid, HCNO; cyanogen, $(CN)_2$; and cyano, CN, shown in Figure 2b for the hearth and combustion zones, are for the following reaction equilibria

$$\frac{1}{2} H_2 + \frac{1}{2} N_2 + C = HCN \qquad (2)$$

$$\frac{1}{2} H_2 + \frac{1}{2} N_2 + CO = HCNO \qquad (3)$$

$$N_2 + 2C = (CN)_2 \qquad (4)$$

$$\frac{1}{2} N_2 + C = CN \qquad (5)$$

Of these cyanides, HCN is the dominant species and forms only at high temperatures.

We may consider two other reactions for the generation of HCN.

$$\frac{3}{2} H_2 + \frac{1}{2} N_2 + CO = HCN + H_2O \tag{6}$$

$$H_2O + N_2 + 5CO = 2HCN + 3CO_2 \tag{7}$$

The calculated equilibrium concentrations of HCN at stack temperatures are shown in Figure 2a: $(HCN)_1$ is for reaction (2), $(HCN)_2$ for reaction (6) and $(HCN)_3$ for reaction (7). All these reactions give relatively small amounts of HCN in the upper part of the stack in comparison to the amounts found in the top gas, indicated by the shaded area.

The concentrations of ammonia in Figure 2a indicated by the subscripts 1, 2 and 3 are calculated for the following reaction equilibria

$(NH_3)_1$: $$\frac{3}{2} H_2 + \frac{1}{2} N_2 = NH_3 \tag{8}$$

$(NH_3)_2$: $$3H_2O + N_2 + 3C = 2NH_3 + 3CO \tag{9}$$

$(NH_3)_3$: $$3H_2O + N_2 + 3CO = 2NH_3 + 3CO_2 \tag{10}$$

Although the generation of ammonia by reaction (8) and (10) are favored at lower temperatures in the upper part of the stack, it is well to remember that these reactions will not occur at these relatively low temperatures in the absence of a suitable catalyst. Therefore, we can rule out the generation of any measurable amount of ammonia by reactions (8) and (10) in the stack.

In all blast furnaces the alkali cyanide vapors are carried into the stack by the ascending furnace gases and condense on the burden as alkali carbonates and cyanides, a phenomenon that has been known in practice since the 1830's.10) The alkali cyanides react readily with water vapor to generate ammonia, thus

$$2K(Na)CN + 3H_2O = (K,Na)_2CO_3 + 2NH_3 + C \qquad (11)$$

The curve marked $(NH_3)_4$ in Figure 2a is calculated for reaction (11) with KCN. The concentration of ammonia in the gas for this reaction increases markedly with decreasing temperature. The amounts of ammonia found in the top gas of iron-blast furnaces correspond to the equilibrium values for reaction (11), with KCN, at stack temperatures of 700 to 750°C.

The ammonia generated by reaction (11) will react with carbon monoxide to form hydrogen cyanide

$$NH_3 + CO = HCN + H_2O \qquad (12)$$

The concentration of hydrogen cyanide designated $(HCN)_4$ in Figure 2a is calculated for the stack gas compositions for reactions (11) and (12). For these reaction equilibria and the stack-gas compositions, the concentration ratio HCN/NH_3 in the gas decreases from about 0.14 at 800°C to about 0.01 at 600°C. In the wash water for the off-gas, the molar ratio HCN/NH_3 varies from 0.01 to 0.1, depending on the size and the operating practice of the blast furnace.

In the upper part of the stack there are other gas-solid reactions which would oppose the formation of ammonia and hydrogen cyanide, if the reaction kinetics were favorable. For example, from the point of view of reaction equilibrium, the ammonia is not stable at stack temperatures in the presence of magnetite or hematite. However, as noted in the present experimental work discussed later, the ammonia in the simulated stack-gas mixtures is not readily oxidized by the higher oxides of iron at temperatures below 600°C.

Experiments

In the light of the foregoing theoretical considerations, based on the reaction thermodynamics, the apparatus was built to study experimentally the state of some of the gas-solid and gas-gas reactions under partially simulated conditions of the upper part of the blast-furnace stack.

Apparatus

The apparatus (Figure 3) consisted of a reaction vessel, a steam generator, a metering manifold for inlet gases and a gas chromatograph for the analysis of inlet and exit gases.

The gas-input metering manifold was simply an array of rotometers calibrated for various gases involved in the experiments, N_2, CO, CO_2, and NH_3.

The reaction vessel, inserted in a wire-wound resistant heating tube, was fabricated from recrystallized alumina tubes. The outer tube, 150 cm in length and 7.6 cm in diameter, was capped at the ends with modified high vacuum Varian flanges by an Epoxy cement. The insert tube that contained the sample was 86 cm in length and 5 cm in diameter. This tube was capped at the base with an alumina disc that had been bored with 3-mm-diameter holes to allow gas to pass up through the packed bed of granulated sample. The top was fitted with a Varian flange to mate with the outer tube. Stainless steel caps and silicone rubber gaskets completed sealing of the reaction vessel by nuts and bolts. Two alumina tubes, 6 mm in diameter, for the thermocouple and gas outlet were attached to the top plate by swagelock fittings.

A steam generator was made for controlled addition of water vapor into the gas stream. A 38 mm diameter stainless steel pipe 300 mm in length was filled with 6 mm nickel balls. The pipe was insulated and wrapped with nichrome wire for heating purposes, and the capped pipe was encased in a 150 mm diameter aluminum cylinder packed with insulating beads and sealed at the ends. Water and gas were simultaneously introduced into the inlet of the steam generator operating at 170°C. A syringe pump was used to admit water through a nickel capillary tube about one-third of the distance inside the heated chamber and allowed the water vapor to mix with the gas as it flowed through the vaporizer chamber.

The absorption column in the gas chromatograph was packed with Poropak PPR, 80 to 100 mesh, treated with 5 percent PEI, operating at 105°C with 30 cc/min helium carrier. This technique effectively separated all the components of interest in the order N_2, CO, CO_2, NH_3 and H_2O in 10 minutes. The limit of detection of NH_3 was about 15 ppm and for $H_2O < 0.1$ percent. The gases did not deteriorate the column and results were reproducible. The sampling was accomplished using gas chromatograph-valving techniques, directly on line with the gas flow. All gas lines were wrapped-stainless steel tubing and heated to 150°C throughout the system.

Experimental Procedure

A charge of various constituents containing 100 g iron ore pellets and/or 50 g dry coke, all crushed and sized to approximately 6 mm, was mixed with 4 g KCN and placed inside the inner tube of the reaction vessel on a bed of silica wool. The entire system was then sealed and He-leak tested. The reaction vessel was heated to the desired temperature with a 50 cc/min N_2 flow. The temperature was uniform over the length of the packed-bed in the reactor. The exit gas was passed through a 0.02N solution of NaOH to absorb hydrogen cyanide; although slightly alkaline, the ammonia in the exit gas was also absorbed by this solution.

In tests for ammonia generation, most experiments were made with two types of inlet gas mixtures: $6\%H_2O + 94\%N_2$ and $28\%CO + 12\%CO_2 + 8\%H_2O + 52\%N_2$. To test the extent of dissociation of ammonia in the reactor, a series of experiments were made with gas mixtures containing about 1 vol-$\%NH_3$. In all the experiments the total gas flow through the reactor was at the rate of 500 cc/min.

Results

As is seen from typical experimental results in Figure 4, for the reactor temperature at 600°C, some ammonia is generated when an H_2O-containing gas mixture is passed through the reactor containing KCN. The concentration of ammonia in the exit gas reached a maximum after some reaction time then decreased at longer reaction times. In the absence of iron oxide in the reactor, the concentration of ammonia in the exit gas continued to increase with the reaction time. Over the reaction times investigated, the amount of KCN consumed in the generation of ammonia by reaction (11) was only a few percent of 4 g KCN in the reactor. Decay in the rate of ammonia generation at longer reaction times is attributed partly to the buildup of the reaction product K_2CO_3 on the KCN particles in the packed bed. At the reactor temperatures in these experiments, the potassium cyanide dissociates by reaction with the iron oxide. It is primarily for this reason that the ammonia generation by reaction (11) decays and ultimately ceases at longer reaction times. In fact, after the completion of ammonia generation, there was only a trace amount of KCN left in the contents of the reactor.

In order to determine the threshold temperature for the onset of reaction (11) to generate ammonia, an experiment was made with increasing and decreasing reactor temperature. As is seen from the results in Figure 5, with the inlet gas mixture 7 vol-%H_2O + 93 vol-%N_2 passing through the reactor containing a mixture of Fe_2O_3, coke and KCN, there was virtually no ammonia generation at 400°C. The ammonia generation was detectable at about 500°C and became appreciable near 600°C. As the temperature was decreased, the concentration of ammonia in the exit gas decreased. The curve in Figure 5 for decreasing reactor temperature is almost a mirror image of that for increasing reactor temperature, indicating reproducibility in the change of rate of reaction with change of temperature.

For a given concentration of water vapor in the inlet gas, the concentration of water vapor in the exit gas, measured by the gas chromatograph, decreased with increasing amounts of ammonia generation as indicated by the stoichiometry of reaction (11). It was also found that with the H_2O-N_2 inlet gas mixtures, the ammonia generation in the reactor containing KCN was accompanied by some CO_2 evolution as indicated by the analysis of the exit gas. The experimental data for the exit gas composition in Figure 6 are for the inlet gas containing 7 vol-%H_2O and 93 vol-%N_2 in three sets of experiments: increasing temperature, decreasing temperature and the isothermal experiments at 600°C. As the concentration of water vapor in the exit gas decreases, i.e. as more ammonia is generated, the concentration of CO_2 in the exit gas increases. The carbon formed by reaction (11) at these moderate temperatures is expected to be in a highly reactive state, hence would readily react with Fe_2O_3 or Fe_3O_4 in the reactor to generate CO and CO_2.

In the system investigated, there are several competing reactions occurring at different rates. For example, the ammonia generated by reaction (11) would be oxidized completely if the reaction kinetics were favorable. To test the extent of oxidation of ammonia a series of experiments were made with the inlet gas mixture H_2O - N_2, containing about 1 vol-%NH_3, passing through the reactor packed with coke, iron oxide or manganese oxide. The experimental results are plotted in Figure 7. The pyrolusite ore (~90% MnO_2) readily oxidizes ammonia at 400°C, because of easy liberation of oxygen from MnO_2; at atmospheric pressure of O_2 and 450°C it dissociates to the lower oxide Mn_2O_3. With Mn_3O_4 there is only partial oxidation of ammonia as it passes through the reactor. The extent of oxidation of ammonia by the iron and lower manganese oxides and thermal decomposition on coke decreases markedly with an increase in the concentration of water vapor in the inlet gas. It is interesting that the water vapor necessary to generate ammonia by reaction (11) also retards the oxidation of ammonia by the iron oxide. The effect of temperature on the extent of oxidation of ammonia (in dry inlet gas mixture) by iron oxide is shown in Figure 8 for two types of charge materials in the reactor. The observed temperature effect is as would be expected.

In the light of the experimental findings with pyrolusite shown in Figure 7, to test the effectiveness of manganese ore in suppressing the ammonia evolution, when added to the blast-furnace burden in relatively small amounts, an experiment was made with the reactor packed with equal volume portions of crushed hematite pellets and coke mixed with 5 percent manganese ore plus 4 g KCN. As already seen from the results in Figure 4 (points ●), no beneficial effect was observed in the suppression of ammonia evolution. That is, small amounts of manganese ore that may be added to the blast-furnace burden would not be sufficient to have any measurable effect on the amount of ammonia, hence cyanide, evolution from the stack.

Discussion

From the composition of the inlet gas and the chromatographic analysis of the exit gas for CO_2 and H_2O, an estimate could be made of the state of the water-gas shift reaction in the reactor filled with hematite and coke. The equilibrium constant K for reaction (1) is 2.7 at 600°C. The values of K derived from the material balance on inlet and exit gas compositions in experiments at 600°C were in the range 2.4 to 3.0, indicating that the composition of the exit gas from the reactor was close to the equilibrium value for reaction (1).

When the gas mixture containing CO and CO_2 was passed through the reactor packed with hematite and coke (with or without KCN), the ratio CO/CO_2 of 7/3 in the inlet gas mixture decreased to about 1:1 in the exit gas. At a position in the blast furnace stack corresponding to a temperature of 600°C, the ratio CO/CO_2 is about 2:1 (Figure 1) which is about twice that found in the present experiments. The superficial gas velocity in these experiments is much lower than that in the blast furnace stack, hence the CO/CO_2 ratio in the gas exiting from the reactor would be lower than that in the blast furnace stack for the same temperature.

The equilibrium constant for reaction (11) (for KCN) at 600°C is $K = (p_{NH_3})^2/(p_{H_2O})^3 = 543\ bar^{-1}$. The values of K obtained from the composition of the exit gas were about one-tenth of the equilibrium value. That is, for the measured concentration of water vapor in the exit gas in the range 2 to 3 percent, the amounts of ammonia generated in the reactor were about one-third of the equilibrium values for reaction (11).

In experiments with CO in the inlet gas and KCN in the reactor, the collector alkaline solution for the exit gas was analyzed for total cyanide content at the termination of the experiment. In a reaction time of two hours, with a total gas flow rate of 500 cc/min, the collector solution contained 3 to 6 mg total CN, depending on the amount of ammonia generation. Assuming that the total cyanide in the collector solution was in the form of HCN gas in the reactor, an estimate could be made of the average concentration of HCN in the reactor during ammonia generation. From the material balance for the inlet and exit gas compositions average values are estimated for the concentrations of H_2O, CO and NH_3 for the two-hour reaction time. The equilibrium constant for reaction (12) at 600°C is $K = (p_{H_2O})(p_{HCN})/(p_{CO})(p_{NH_3}) = 0.0014$. The values of K derived from the average exit gas compositions were in the range 0.001 to 0.002, indicating that the state of reaction (12) in the reactor was near equilibrium.

For the average gas composition in the iron blast-furnace stack given in Figure 1, the equilibrium molar concentration ratio HCN/NH_3 would be about 0.025 at 600°C, 0.042 at 700°C and 0.087 at 800°C. The analyses of wash-water for the iron blast-furnace off gas give molar ratios HCN/NH_3 usually in the range 0.04 to 0.06, which are the equilibrium values for temperatures of 700 to 750°C.

It is all too clear from the experimental results of the present investigation that the presence of alkali cyanides in the blast-furnace stack is responsible for the formation of ammonia and volatile cyanides (mostly HCN) in the upper part of the stack. Many theoretical and experimental studies have been made in the past of alkali recycle in the blast furnace and deposition of alkali cyanides and carbonates on the burden and the refractory lining of the furnace stack; these are discussed in the references cited.11,12) In the light of the present findings, further development may be made of our understanding of reactions responsible for the alkali cycle in the blast furnace.

Alkali Cyanides in Blast-Furnace Stack

General concensus evolved from elementary thermodynamic calculations is that the alkali silicates in the ore and coke ash decompose at elevated temperatures in the lower part of the bosh and the combustion zone. In part the alkali vapors carried away with the ascending gas react with the slag and can therefore be removed from the furnace; part are converted to alkali carbonates and cyanides and deposited on the burden in the stack and on the refractory lining.

The equilibrium vapor pressure of potassium for the slag is calculated by considering the reduction reaction

$$(K_2O) + C = 2K(g) + CO(g) \qquad (13)$$

for which the equilibrium constant for unit activity of carbon (for graphite-saturated melts) is represented by

$$K = \frac{(p_K)^2 \; p_{CO}}{a_{K_2O}} \qquad (14)$$

where the gas partial pressures, p, are in bar and a_{K_2O} is the thermodynamic activity of K_2O in the slag relative to the hypothetical solid K_2O. Steiler[13)] measured the activity of K_2O in potassium silicate melts and blast-furnace type slags at temperatures of 1300 to 1600°C. Using these activity data and the equilibrium constant K derived from the thermochemical data,[9)] the potassium vapor pressures are calculated as a function of temperature for a slag containing 0.5%K_2O, ~7%MgO, ~12%Al_2O_3 with basicity $(CaO + MgO)/SiO_2 = 1.5$; the results are given in Table I for 1.3 bar partial pressure of CO.

Table I. Equilibrium Vapor Pressure of Potassium for a Blast-Furnace Type Slag Containing 0.5%K_2O

Temperature, °C	K, bar^3	a_{K_2O}	p_K, bar
1200	3.10×10^5	2.1×10^{-12}	7.1×10^{-4}
1300	2.69×10^6	5.5×10^{-12}	3.4×10^{-3}
1400	1.81×10^7	1.4×10^{-11}	1.4×10^{-2}
1500	9.78×10^7	3.5×10^{-11}	2.6×10^{-1}

As an example, let us take for the potassium input with the blast furnace burden being 4 kg K/t HM. If 80 percent of the potassium input is removed by the slag, about 0.8 kg K/t HM will be in the vapor phase carried away by the furnace gas. Assuming that the total gas volume is 2300 nm^3/t HM, the partial pressure of the total potassium vapor species would be 7.2×10^{-4} bar (for a total gas pressure of 3.6 bar in the bosh region). Comparison of this total potassium vapor pressure in the gas with that for the slag in Table I indicates that the slag will pick up potassium from the gas only at temperatures below 1200°C. It is evident from these numerical examples that much of the potassium accumulated in the bosh and hearth zone of the blast furnace, via recycling, is in the gas phase.

According to a mass spectrometric study of vaporization of potassium cyanide by Simmons et al,14) the most dominant vapor species are the monomer KCN and the dimer $(KCN)_2$; the trimer $(KCN)_3$ being the least significant vapor species. They measured the vapor pressure of solid KCN over the temperature range 493 to 617°C, and using the estimated heat of fusion, 14.64 kJ mol^{-1} at the melting temperature of 635°C, they obtained the following equations for the vapor species in equilibrium with molten KCN, the pressure being in bar

$$\log p_{KCN} = \frac{-10,500}{T} + 6.704 \qquad (15a)$$

$$\log p_{(KCN)_2} = \frac{-11,405}{T} + 8.011 \qquad (15b)$$

$$\log p_{(KCN)_3} = \frac{-13,700}{T} + 8.067 \qquad (15c)$$

For the reaction

$$K\ (g) + C\ (s) + \frac{1}{2}\ N_2\ (g) = KCN\ (g) \qquad (16)$$

at unit carbon activity and 1 bar pressure of N_2 (an average value in the blast-furnace stack), the equilibrium ratio p_{KCN}/p_K in the stack gas is derived from equation (15a) and the compiled free energy data for liquid KCN for temperatures between the melting point 635°C and the boiling point 1132°C, as given below

$$\log \frac{p_{KCN}}{p_K} = \frac{-1540}{T} + 1.818 \qquad (17)$$

The equilibrium partial pressure ratios $(KCN)_2/KCN$ and KCN/K calculated from equations (15a), (15b) and (17) are plotted in Figure 9 as a function of temperature. It is seen that for these vapor species the equilibrium pressures are in the following decreasing order: $p_{(KCN)_2} > p_{KCN} > p_K$; that is, $(KCN)_2$ is the dominant vapor species containing potassium, particularly at elevated temperatures.

The sodium in the burden undergoes cyclic reactions similar to those discussed above for potassium. However, the thermochemical calculations show that the concentration of sodium-bearing vapor species are about one-tenth of the potassium-bearing species.

As the potassium and potassium cyanide vapors are carried to the cooler parts of the stack they react with CO and CO_2 and condense as liquid or solid (<901°C) carbonate, thus

$$(KCN)_2 + 4CO_2 = K_2CO_3\ (\ell,s) + 5CO + N_2 \qquad (18)$$

$$(KCN)_2 + 3CO = K_2CO_3\ (\ell,s) + 3C + N_2 \qquad (19)$$

The equilibrium partial pressures of $(KCN)_2$ calculated for these reactions for stack gas compositions (Figure 1) are compared in Figure 10 with the vapor pressure of liquid KCN. If the kinetics of reactions (18) and (19) are favorable, most of the potassium-bearing volatile species will condense as potassium carbonate at temperatures in the lower part of the stack. Under such conditions, there would be little or no condensation of KCN in the upper part of the stack, hence no generation of NH_3 and HCN by reactions (11) and (12). The fact that these reactions do occur in the upper part of the stack at temperatures of 750 to 700°C, as substantiated by the present experiments and the plant data, suggests that the rates of reactions (18) and (19) are sluggish, thus permitting the ascent of KCN vapors to the upper part of the stack. Ultimately, however, more potassium carbonate would form by reaction of potassium cyanide with water vapor, resulting in ammonia generation as in reaction (11). The range for the $(KCN)_2$ pressure in the stack shown by broken lines in Figure 10 is estimated from the ammonia contents of the blast furnace-top gas (Figure 2) and average stack-gas compositions by assuming equilibrium for reaction (11).

Because of the countercurrent flow of solids and gases, and the cyclic sequence of condensation and vaporization reactions, some alkali cyanides are always present in the upper part of the stack, resulting in continuous generation of NH_3 and HCN by reactions (11) and (12). In the ferromanganese-blast furnace the stack temperatures are higher than those in the iron-blast furnace. Therefore, more alkali cyanides will be carried to the upper part of the stack, hence more NH_3 and HCN will be generated in the ferromanganese-blast furnace in comparison to the iron-blast-furnace as noted in practice.

Conclusions

The results of the present experimental study, under partially simulated conditions of the blast-furnace stack, have substantiated the view that the volatile alkali cyanides carried by the furnace gas are responsible for the generation of ammonia and hydrogen cyanide in the upper part of the stack

$$2K(Na)CN + 3H_2O = (K,Na)_2CO_3 + 2NH_3 + C$$

$$NH_3 + CO = HCN + H_2O$$

Other reactions will occur with these volatile species generating some amino-nitro phenols, e.g. $NH_2(NO_2)C_6H_3OH$. The equilibrium concentrations of these volatile organic species become greater at lower temperatures. In the present experimental conditions, the threshold temperature for the onset of ammonia generation was about 500°C; the reaction occurred rapidly at temperatures above 580°C. For the gas compositions used in the experiments, partially simulating the conditions in the blast-furnace stack, the amount of ammonia generated was about one-third of the equilibrium value for reaction of KCN with H_2O. However, the ratio HCN/NH_3 in the gas exiting the reactor at 600°C was close to the equilibrium value for reaction of NH_3 with CO to yield HCN and H_2O. The composition of the exit gas also indicated close approach to equilibrium for the water gas shift reaction in the reactor at 600°C.

In blast furnaces operating with slags of high basicity, more alkali cyanide vapors will be carried into the stack, hence will result in more ammonia and hydrogen cyanide in the upper part of the stack. The thermochemical calculations have shown that $(KCN)_2$ and KCN are the primary vapor species of the alkali-bearing vapors in the stack; the higher the temperature the greater the equilibrium partial pressure of $(KCN)_2$. The stack temperatures and slag basicities in the ferromanganese-blast furnace are higher than those in the iron-blast furnace. Therefore, in the ferromanganese blast furnace there will be more carry-over of alkali cyanide vapors to the stack, resulting in the generation of more volatile matter compared to the iron-blast furnace; such a deduction is in accord with plant observations.

Coke quenched with contaminated coke plant waste water contains cyanides and ammonia which in turn will contribute to the generation of volatile matter in the stack. This is again in accord with plant observations.

Because of unfavorable reaction kinetics at stack temperatures, the magnetite, hematite and additions of manganese ore to the simulated blast-furnace burden, in the present experiments, were not effective in suppressing the formation of ammonia and hydrogen cyanide. For a partial remedy of this problem in practice, the coke in the burden should be free of the cyanide contamination, the alkali input with the burden should be kept to a minimum and the carry-over of alkali cyanide vapors to the stack be curtailed by operating the furnace with a slag of low basicity that is permissable for an acceptable sulfur level in the hot metal.

Acknowledgment

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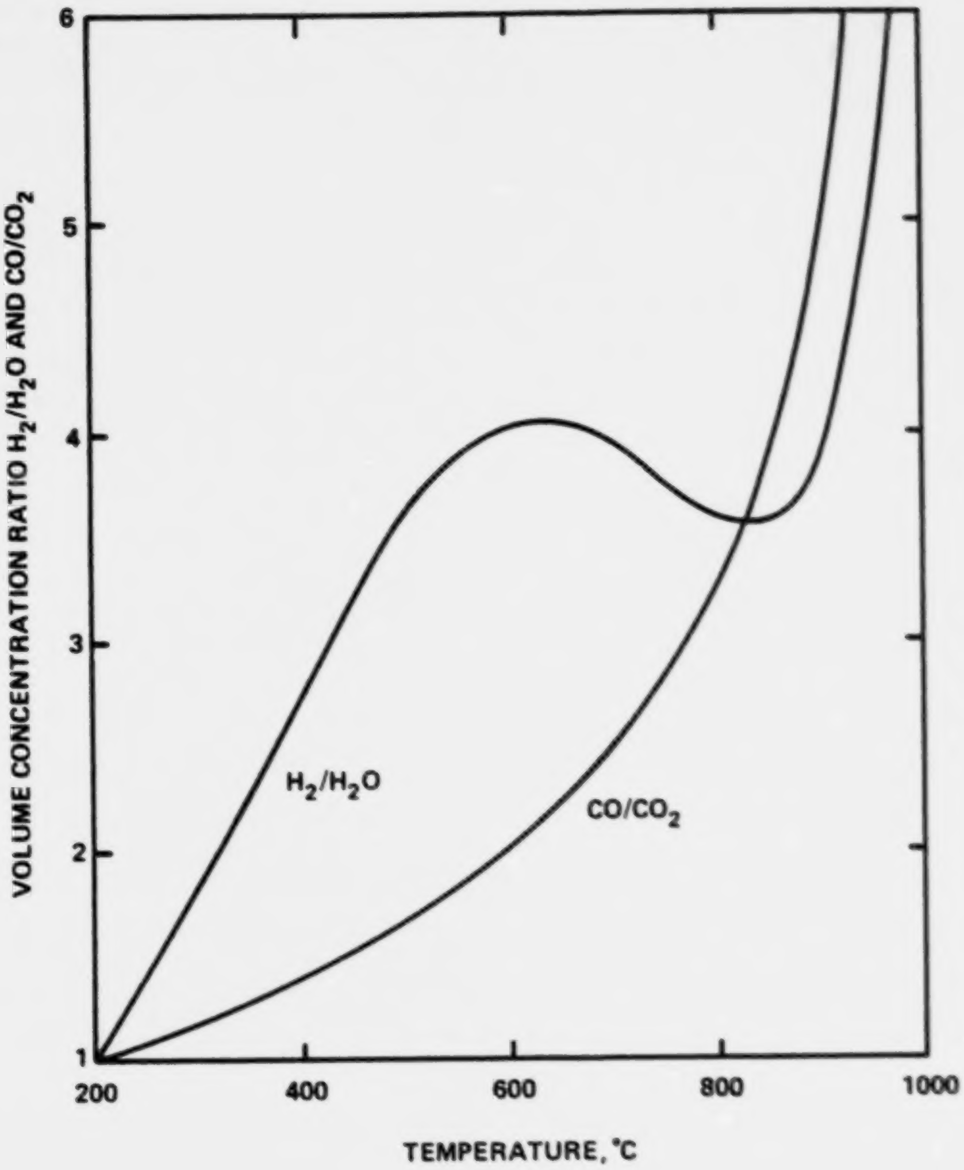

Figure 1 GAS CONCENTRATION RATIO H_2/H_2O AND CO/CO_2 IN THE IRON BLAST FURNACE STACK

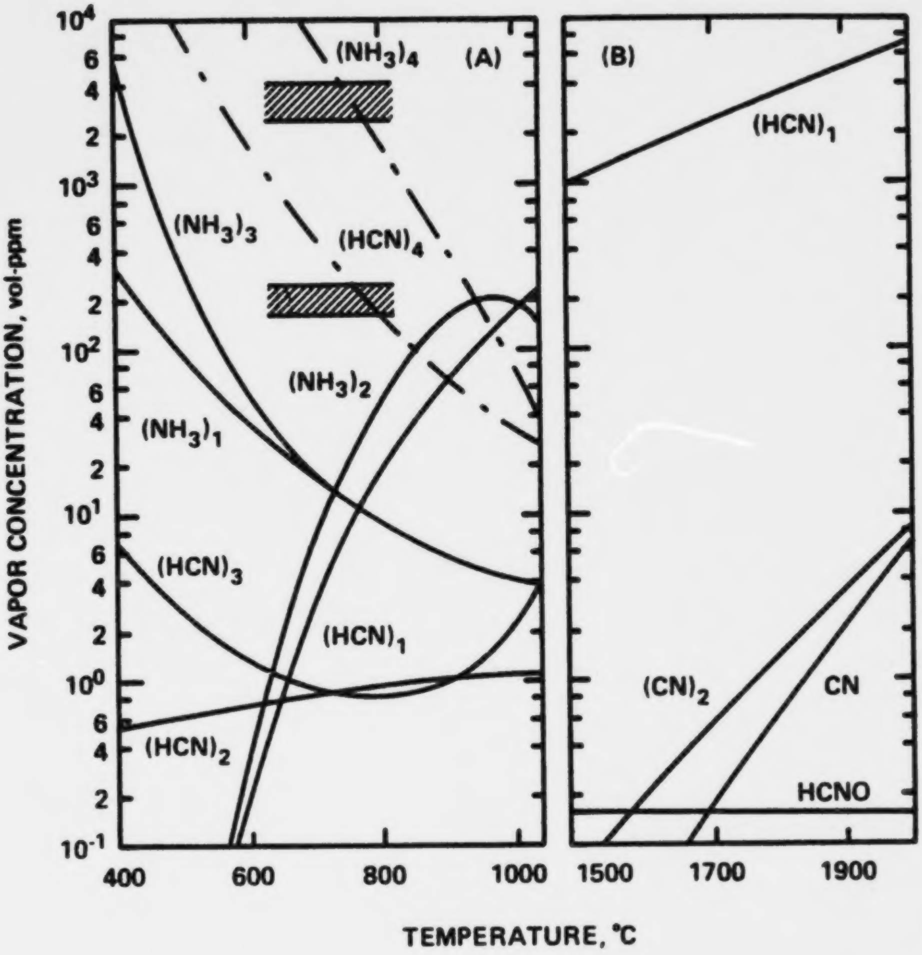

Figure 2 EQUILIBRIUM CONCENTRATIONS OF AMMONIA AND CYANIDES CALCULATED FOR VARIOUS REACTIONS IN THE (A) STACK AND (B) HEARTH AND COMBUSTION ZONE OF THE IRON BLAST FURNACE; SHADED AREAS ARE AVERAGE CONCENTRATIONS OF AMMONIA AND TOTAL CYANIDES IN DUST-FREE SAMPLES OF BLAST-FURNACE TOP GAS

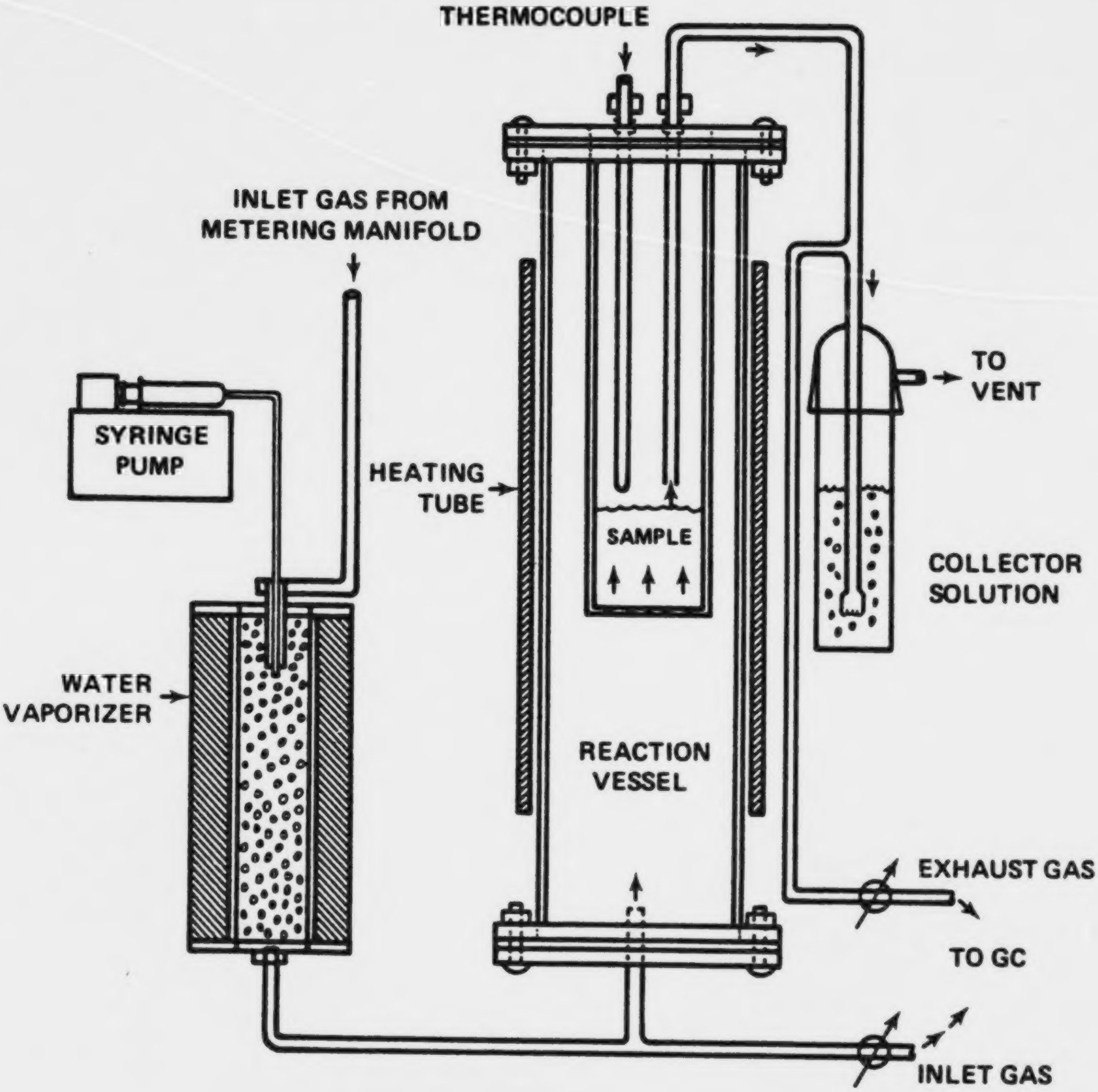
THERMOCOUPLE
INLET GAS FROM METERING MANIFOLD
SYRINGE PUMP
HEATING TUBE
SAMPLE
TO VENT
COLLECTOR SOLUTION
WATER VAPORIZER
REACTION VESSEL
EXHAUST GAS
TO GC
INLET GAS

Figure 3 SCHEMATIC DIAGRAM OF APPARATUS; GC INDICATES GAS CHROMATOGRAPH

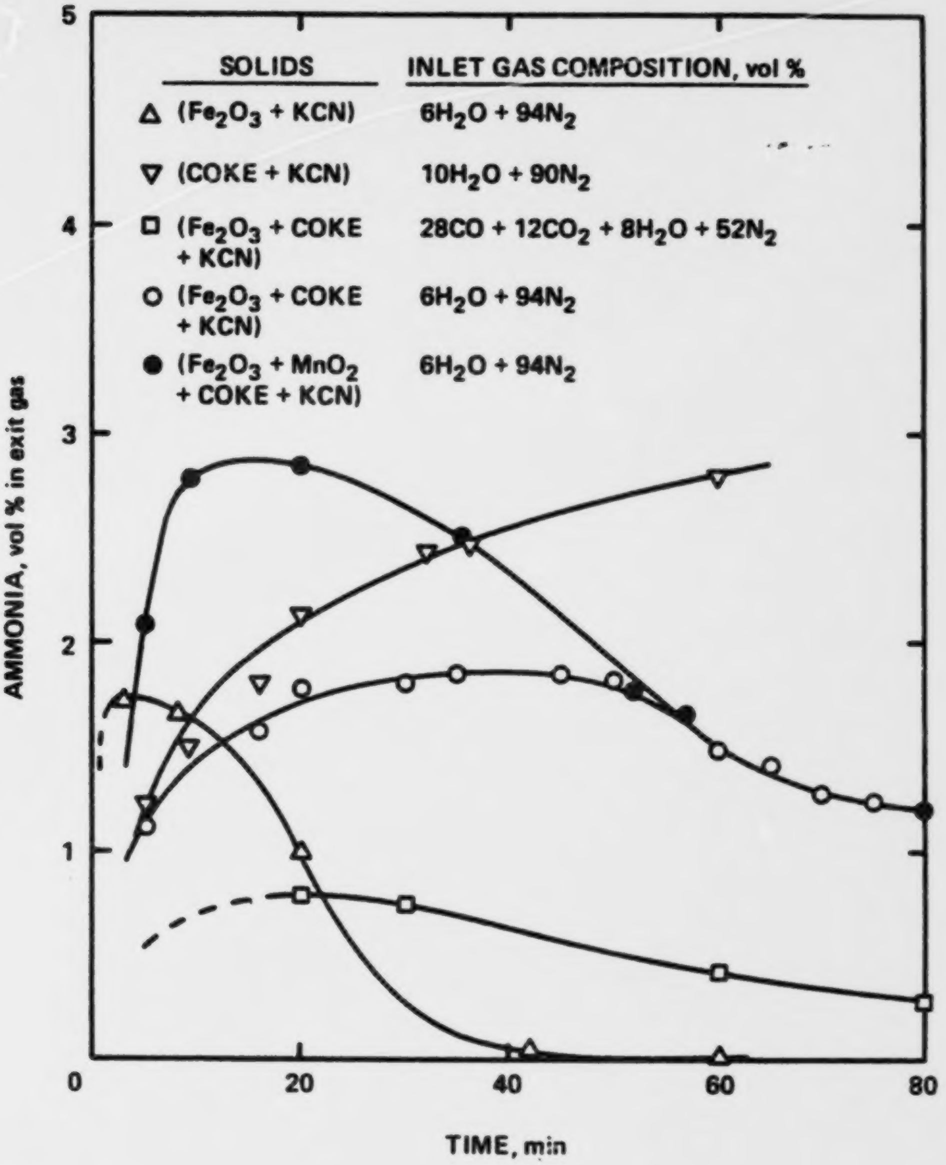

Figure 4 AMMONIA GENERATION AS A FUNCTION OF REACTION TIME AT 600°C FOR VARIOUS KCN-CONTAINING MATERIALS IN THE REACTOR

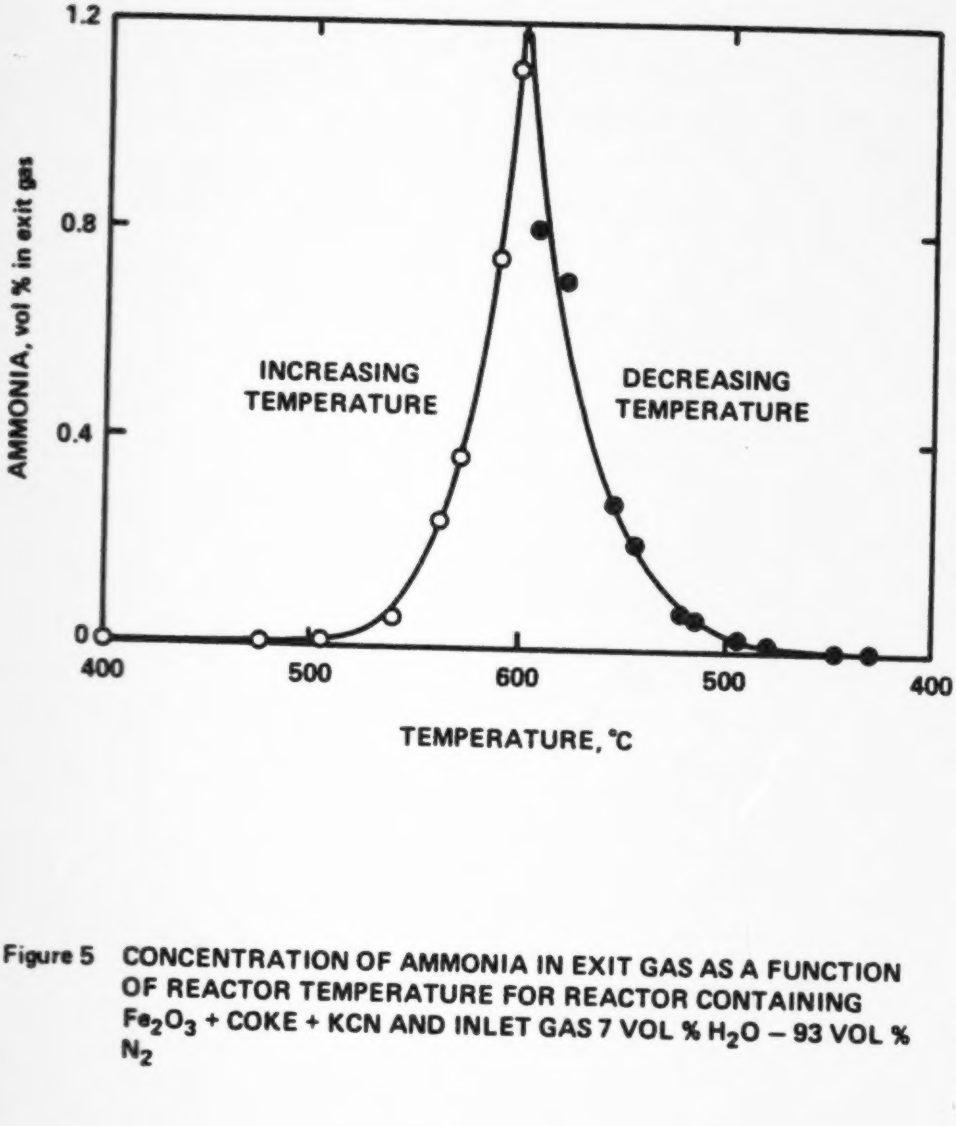

Figure 5 CONCENTRATION OF AMMONIA IN EXIT GAS AS A FUNCTION OF REACTOR TEMPERATURE FOR REACTOR CONTAINING Fe_2O_3 + COKE + KCN AND INLET GAS 7 VOL % H_2O – 93 VOL % N_2

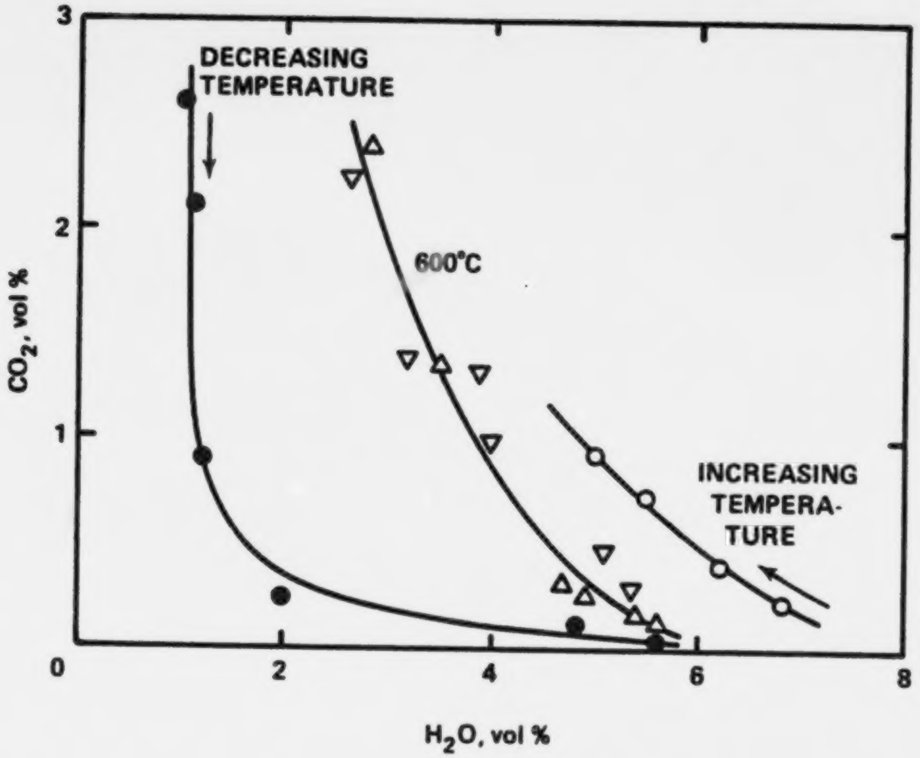

Figure 6 RELATION BETWEEN CONCENTRATION OF CO_2 AND H_2O IN EXIT GAS WHEN AMMONIA IS GENERATED IN THE REACTOR (Fe_2O_3 + COKE + KCN) WITH INLET GAS 7 VOL % H_2O + 93 VOL % N_2; POINTS (▽) ARE FOR REACTOR PACKED WITH Fe_2O_3 + KCN

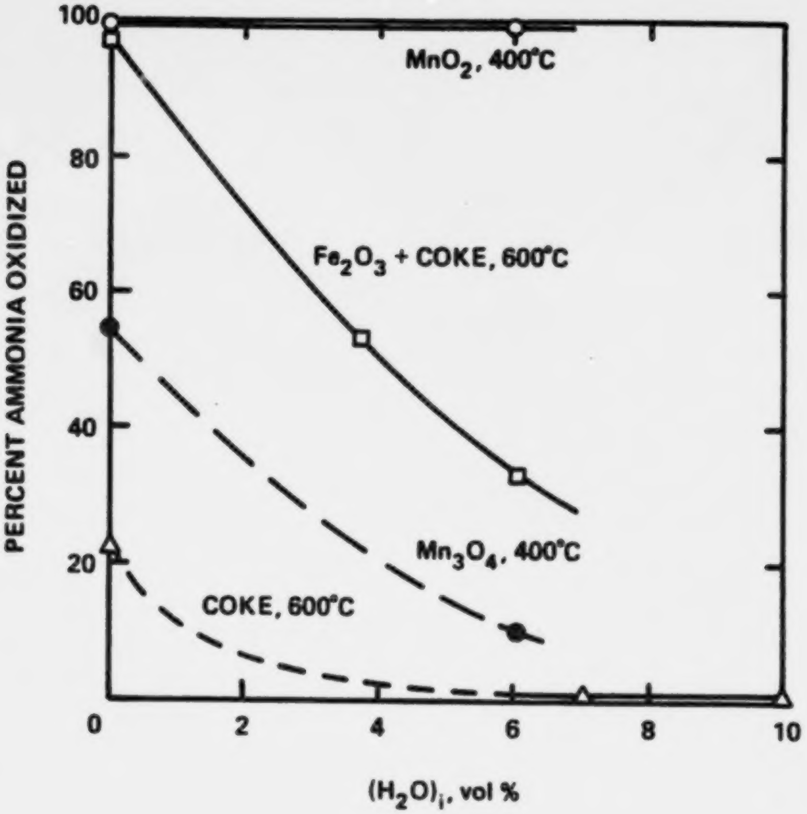

Figure 7 EFFECT OF CONCENTRATION OF H_2O IN INLET GAS N_2-H_2O-~1% NH_3 ON OXIDATION OF AMMONIA IN REACTOR PACKED WITH INDICATED MATERIALS

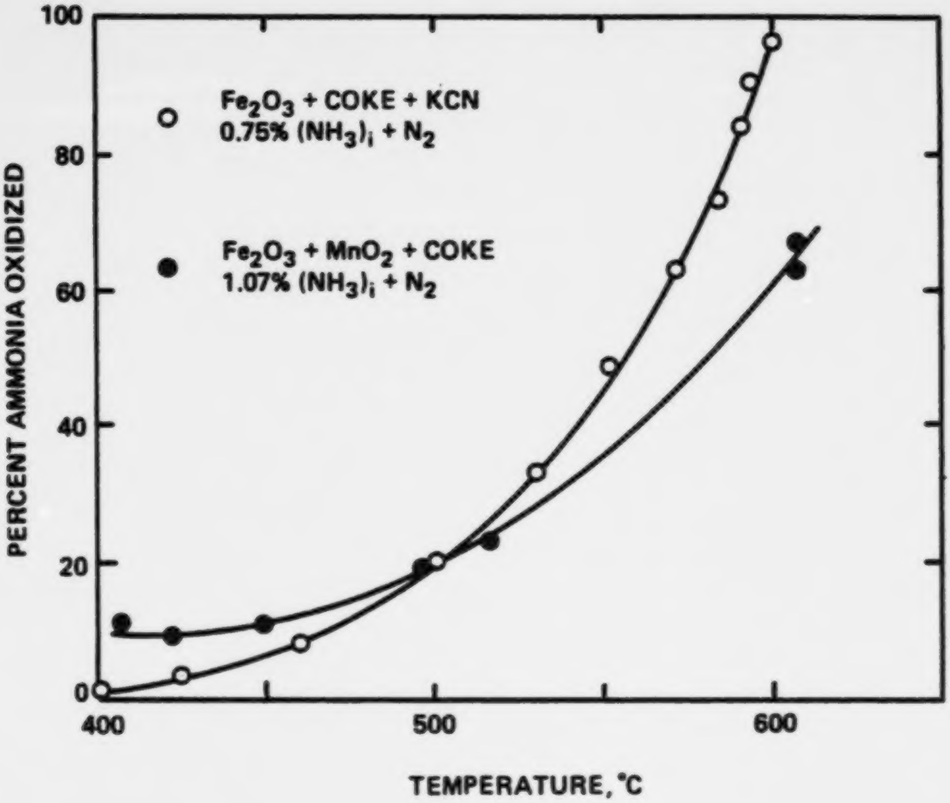

Figure 8 EFFECT OF TEMPERATURE ON OXIDATION OF AMMONIA IN REACTOR PACKED WITH INDICATED MIXTURES OF MATERIALS

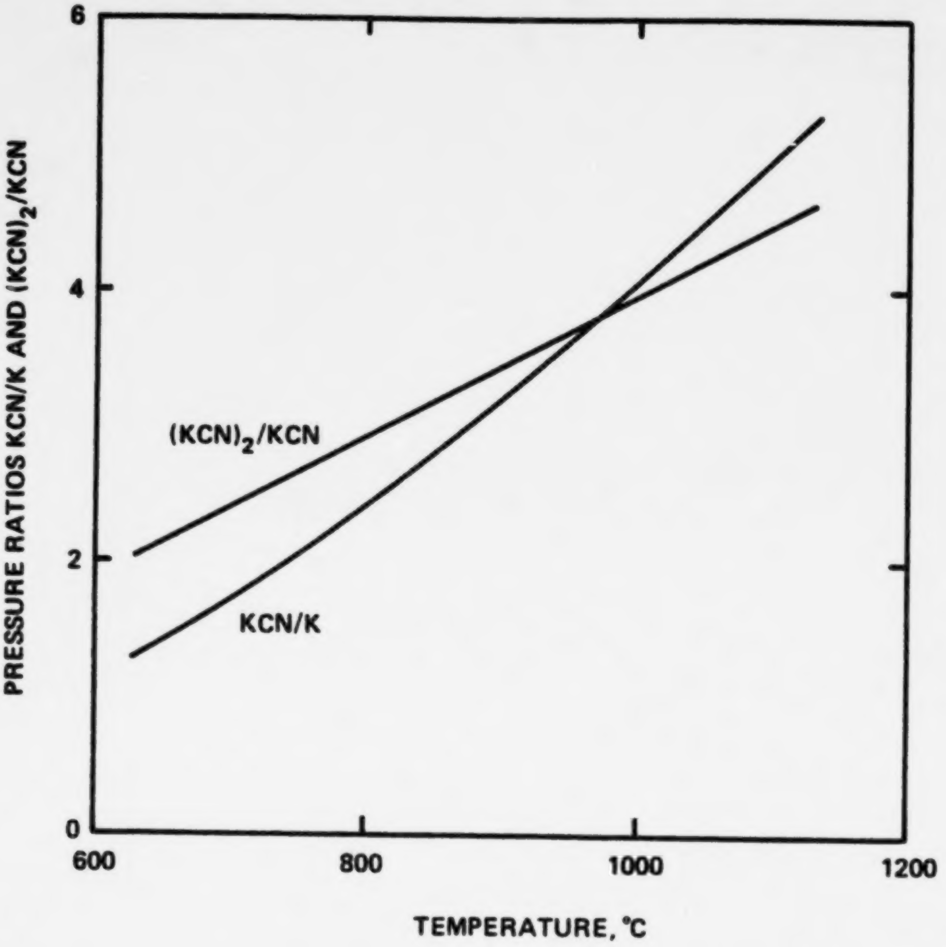

Figure 9 CALCULATED VAPOR PRESSURE RATIOS KCN/K AND (KCN)$_2$/KCN FOR UNIT CARBON ACTIVITY AND ATMOSPHERIC PRESSURE OF NITROGEN FOR TEMPERATURES BETWEEN MELTING POINT (635°C) AND BOILING POINT (1132°C) OF POTASSIUM CYANIDE

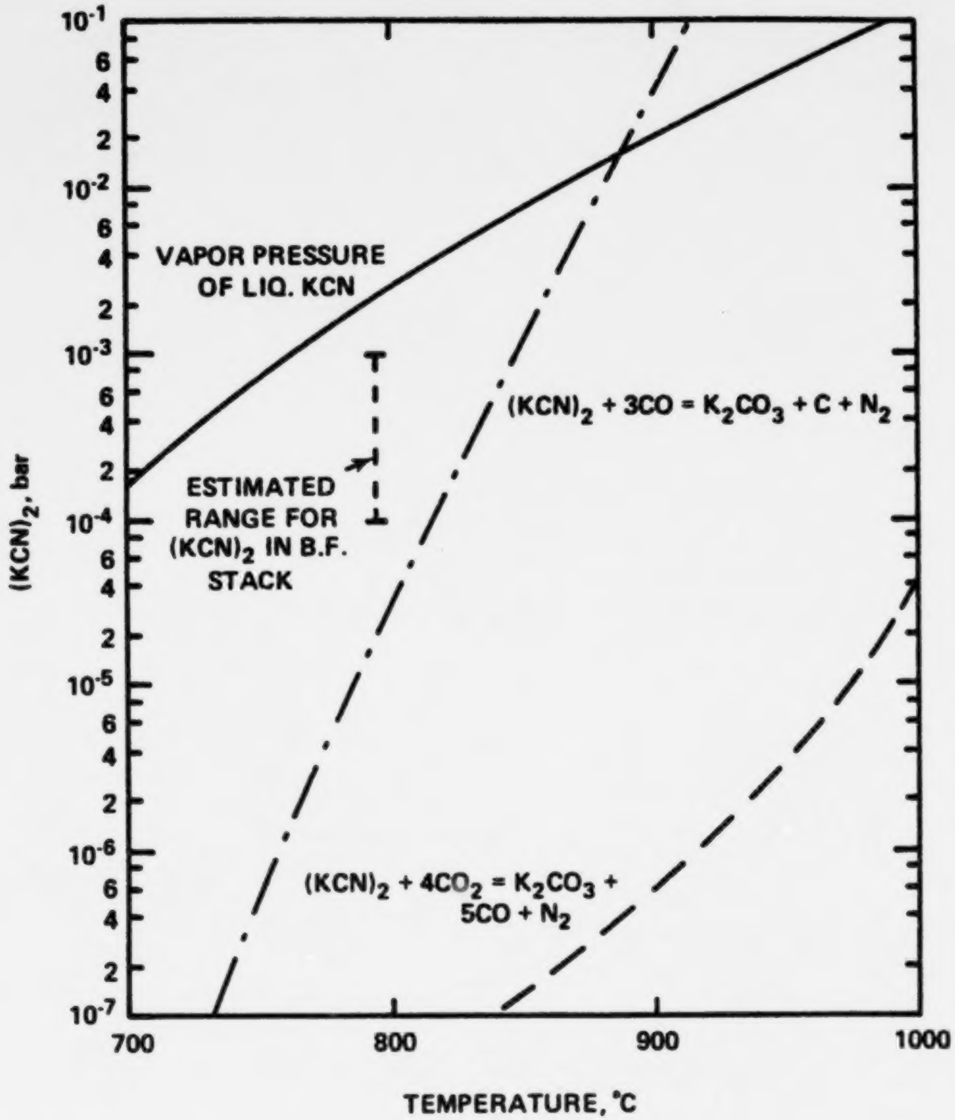

Figure 10 CALCULATED $(KCN)_2$ PRESSURES FOR INDICATED REACTIONS IN BLAST FURNACE STACK ARE COMPARED WITH THE VAPOR PRESSURE OF LIQUID KCN

THE IMPACT OF IRON AND STEEL PLANTS ON RIVER WATER QUALITY

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ABSTRACT

This paper summarizes data generated in 1982 for major rivers from the upper Ohio River Basin in the Pittsburgh area and the lower Cuyahoga River in the Cleveland area. The Ohio River Basin data includes water analyses from four locations on the Monongahela River, four on the Kiski and Allegheny Rivers, and four on the Ohio River. The Cuyahoga River data is from two locations. Sampling stations were located above and below operating steel plants. The data base established will be used for determinations of long term trends, and for projection of the extent to which river water quality will be affected by the implementation by the steel industry of Best Available Technology effluent guidelines on top of technology and practices already installed.

Up to 16 physical and chemical parameters were monitored, including temperature, pH, hardness, TSS, ammonia, free cyanide, total cyanide, phenolics, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc. Production data on coal coked and hot metal produced, and river flow data were also obtained.

Many of the analytical results obtained were at or below the detection limits of the analytical methods. Overall, the steel industry impact on river water quality was minimal for 1982 plant operating and river flow conditions.

INTRODUCTION

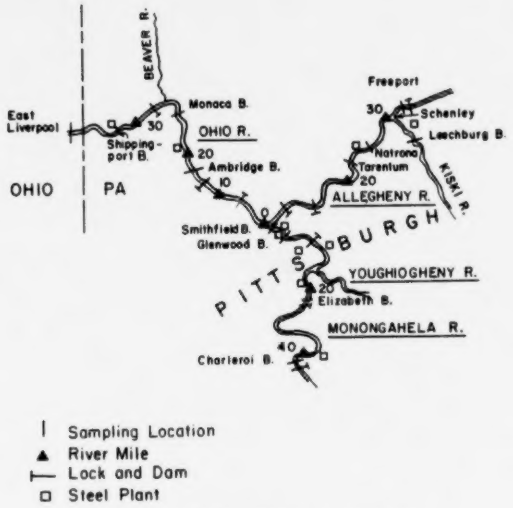
This project was undertaken to develop a data base of ambient water quality in river basins which receive steel plant process wastewater discharges. The data base will be used for assessment of water quality benefits projected to result from the implementation by the steel industry of Best Available Technology (BAT) on top of the Best Practicable Technology (BPT), which in many cases has already been installed.

The steel industry has already made great progress in meeting the regulations stemming from the Clean Water Act of 1972, and its Amendments of 1977. Based on Environmental Protection Agency (EPA) estimates, by meeting the BPT guidelines the steel industry will have reduced its raw effluent loadings of regulated pollutants by over 98%. To accomplish this high reduction, the industry has made capital expenditures of $1.412 billion over the past ten years. Further large expenditures will be required for moving from BPT to the more restrictive BAT guidelines. Widely different estimates of these additional expenditures have been made by EPA and the American Iron and Steel Institute (AISI). However, an economic cost benefit analyses(1) made for the AISI has shown that the potential benefits accruing by going from BPT to BAT are greatly exceeded by the incremental expenditures, whether EPA or AISI cost estimates are used.

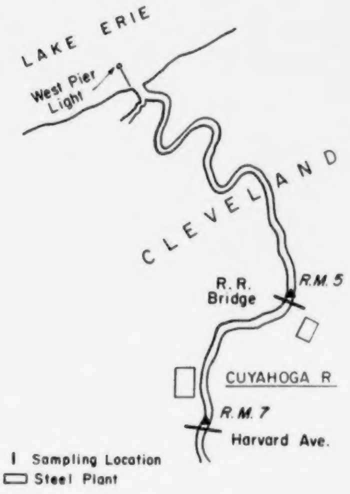
PROCEDURE

To determine present water quality which can serve as a basis for comparing quality changes over time and varying conditions, long-term river sampling and analysis programs were undertaken. Two river basins into which active steel plants discharge their effluents were sampled. The larger area is the upper Ohio River Basin (ORB) around Pittsburgh, PA, including segments around the Monongahela, Kiski, Allegheny, and Ohio Rivers. Five companies sampled 12 locations in this area. These locations are shown in Figure 1. The Charleroi, Freeport, and Leechburg locations are upstream of the steel plants. River miles are measured from the Point in Pittsburgh where the Monongahela and Allegheny join to form the Ohio River. All the ORB study points are in Pennsylvania, except for East Liverpool, which is just over the Ohio border. The second area was a segment of the lower Cuyahoga River in Cleveland, Ohio. Two companies sampled at two locations on the Cuyahoga, as shown in Figure 2. Both of the Cuyahoga study points are in Ohio.

The water quality of the ORB is under regulation by the U.S. EPA, Pennsylvania Department of Environmental Resources (DER), and the Ohio River Valley Water Sanitation Commission (ORSANCO). River water quality standards for the ORB and ORSANCO are listed below. The Cuyahoga is under regulation of EPA and Ohio EPA. The Ohio Warmwater Habitat designation, although it does not apply to the lower Cuyahoga, is in general application in Ohio and is listed below for reference.


BEAVER R.
East Liverpool
OHIO
PA
30
Shipping-port B.
Monaca B.
OHIO R.
20
Ambridge B.
10
Smithfield B.
Glenwood B.
PITTSBURGH
Freeport
30
Schenley
Leechburg B.
Natrona
Tarentum
20
KISKI R.
ALLEGHENY R.
YOUGHIOGHENY R.
20
Elizabeth B.
MONONGAHELA R.
40
Charleroi B.
Sampling Location
River Mile
Lock and Dam
Steel Plant

OHIO RIVER BASIN STUDY AREA
FIGURE 1


LAKE ERIE
West Pier Light
CLEVELAND
R.R. Bridge
R.M. 5
CUYAHOGA R
R.M. 7
Harvard Ave.
Sampling Location
Steel Plant

CUYAHOGA RIVER BASIN STUDY AREA
FIGURE 2

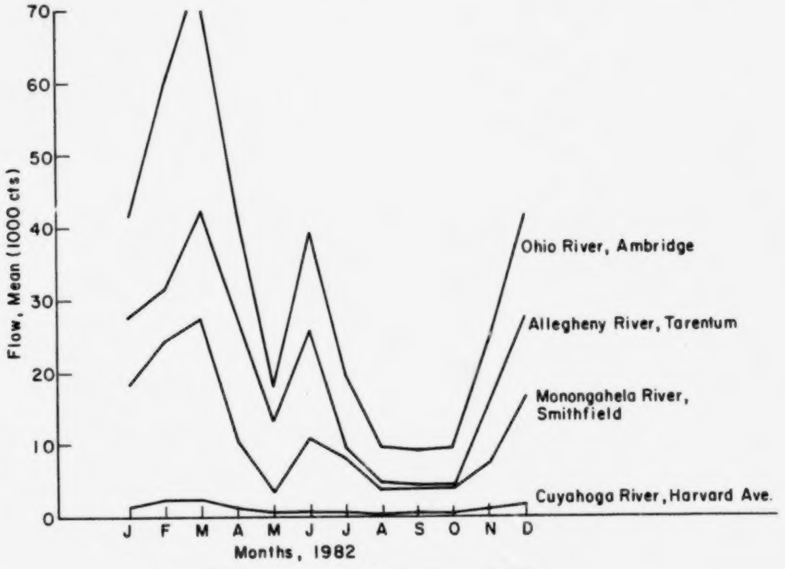


FIGURE 3 Average River Flow, 1982

WATER QUALITY STANDARDS, mg/l

	Ohio River Basin		Ohio EPA
	Pennsylvania	Ohio and ORSANCO	Warmwater Habitat
Cadmium	.010	.010	0.012
Chromium			0.100
Chromium, Hex.	.050	.050	
Copper	0.1 x 96 hr LC50	.1 x 96 hr LC50	0.1 x 96 hr LC50
Cyanide, total	.025 (Ohio R. only)	.025	.025
Cyanide, free	.005		
Lead	.050	.050 (dissolved)	.030
Nickel	.01 x 96 hr LC50		.01 x 96 hr LC50
Phenolics	.005	.010	.010
Selenium	.010	.010	.01 x 96 hr LC50
Zinc	.01 x 96 hr LC50	.1 x 96 hr LC50	.01 x 96 hr LC50

Initially, sampling frequency was set at twice weekly and parameters to be measured were: temperature, pH, total suspended solids, hardness, phenolics, free cyanide, total cyanide, ammonia nitrogen, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc.

River samples were taken by participating steel companies above and/or below their respective plants. The samples were analyzed by laboratories which have been audited by U.S. EPA for water analysis. A protocol, which closely follows procedures given in EPA's "Methods for Chemical Analysis of Water and Wastes", was prepared by the Fellowship and distributed to the participating companies. In addition, two alternate methods, AISI Aeration Method and the Pennsylvania DER Suggested Method were allowed for free cyanide. When possible, all metal parameters were monitored by the atomic absorption technique of direct aspiration. The participants periodically sent their analytical data to the Fellowship for consolidation and inclusion in this report for the year 1982. The participants decreased their frequency of sampling during the year because of the low levels of plant operations and decreases in laboratory personnel, and one company withdrew from the project in April. Many of the analytical values for metals in the ORB were found to be at or below the detection limits. Analyses for such metals were stopped part way through the project.

External factors which determine the effect of steel plant effluents on water quality include river flow rate, pollutant discharge rate, and upstream concentrations. In general, the impact of point source discharges will be greatest at low river flows. At high flow conditions, river water quality violations are frequently the result of non-point sources.

River flow data were obtained from the U.S. Geological Survey for relevant locations closest to the sampling points. The average flow rates for 1982 for the downstream locations were: 34,700 cfs at E. Liverpool on the Ohio, 20,500 cfs at Tarentum on the Allegheny, 11,300 cfs at Smithfield on the Monongahela, and 1,030 cfs on the lower Cuyahoga. Historic records of stream flow in the ORB indicate a normal pattern of lowest flows in September, and highest flows in March. Because of variations in topography and local weather, and flow control through locks and dams, relative flows of the tributaries may vary more than that of the mainstem of the Ohio River. For purposes of providing depth control for navigation, the Corps of Engineers maintains eight locks and dams within the surveyed segment of the Ohio River Basin. The Cuyahoga River, which normally has a relatively low flow rate, runs through a heavily industrialized, highly populated area. Upstream of the steel plants, a very large municipal sewage treatment plant, Cleveland Southerly, discharges into the river. The Cleveland Southerly effluent of 91 million gallons per day accounts for 14% of the average flow of the lower Cuyahoga. The combination of high discharges, annual dredging for navigation, and low river flow makes water quality control difficult in the lower Cuyahoga.

The wide fluctuations in river flow in 1982 is illustrated in Figure 3. The ratio of high to low average monthly flow rate was 8.2 for the Ohio, 10.1 for the Allegheny, 8.1 for the Monongahela, and 10.1 for the Cuyahoga Rivers. The Kiski, a small tributary of the Allegheny which supplies 10% of its flow, had a high to low ratio of 9.5.

The waters in the ORB rivers are used for a variety of beneficial purposes including public water supply, contact and non-contact water-based recreation, industrial process and cooling water supplies, propagation and growth of aquatic life, navigation and transport of industrial and municipal wastewaters. The waters in the ORB are protected for warm water fish and navigation purposes. The lower Cuyahoga River is classified as appropriate for industrial water supply and secondary contact recreational purposes.

The rivers in this study receive point source effluent loadings from other industries and municipal treatment plants in addition to steel industry effluents. They also receive large volumes of urban and rural runoff following precipitation or snow melt. The contributions of sources other than the steel industry are not defined in this study.

DATA HANDLING

Many of the analytical results were reported as below the detection limits (bdl) of the analytical methods. Different detection limits for a given parameter were reported by different laboratories, and even a single laboratory reported different detection limits for the same parameters on different dates. Many of the parameters were reported as bdl for a major percentage of the samples. A meaningful average cannot be determined for such pollutants. In the table of analytical results, two average values are reported for parameters which have bdl values. Avg. 1 is calculated with all bdl values assumed equal to the detection limit, and Avg. 2 is calculated with all bdl values assumed equal to zero. The true average will lie between Avg. 1 and Avg. 2.

The mingling of a large number of low and bdl values with a small number of relatively high values, results in a non-normal distribution of data. For such cases, the central tendency of the data points can be better expressed by the median rather than the assumed mean because the median is less sensitive to a few very high or very low values in a set of data.

Coke oven and blast furnace production were taken as indicators of steel industry operations and potential sources of the pollutants being measured. In the ORB, the entire coke and hot metal operations were along the Monongahela and Ohio Rivers. These operations varied throughout the year, with different rate changes at specific locations. The daily rate for coal coked along the Monongahela accumulated to Smithfield Bridge, varied from 3,300 to 13,860 tons per day, and the accumulated rate for the ORB at East Liverpool was 7,470 to 18,760 tons per day. Similar hot metal production rates were 1,800 to 8,310 tons per day at Smithfield and 2,910 to 13,540 tons per day at East Liverpool. Along the Cuyahoga River, between the upstream and downstream points, the daily rate for coal coked varied from 1,880 to 2,880 tons per day, and for hot metal produced from 5,380 to 10,250 tons per day.

DATA ASSESSMENT

OHIO RIVER BASIN

In the Ohio River Basin the following pollutants exceeded PA standards at some time: phenolics, total cyanide, free cyanide, nickel, and zinc. These are listed with their frequency of exceedance at the upstream point and the furthest downstream point for each river in Table 1. The concentrations of ammonia, phenolics, total cyanide, and free cyanide are summarized in Figures 4 to 7. In these figures, the vertical lines show the range of values and the continuous line joins the median values for the sampling locations going down the Monongahela to its juncture with the Allegheny, then proceeding down the Ohio River. The median ammonia concentrations increased along the Monongahela then decreased along the mainstem of the Ohio.

Phenolics concentrations exceeded the PA standard at some time in each of the rivers at both upstream and downstream locations. On the Monongahela the most frequent exceedance and the only median which exceeded the PA standard occurred upstream at Charleroi. An unexplained phenolics concentration of 0.19 mg/l was obtained at Smithfield on 1/18/82. No correspondingly high value was found above or below Smithfield. On the Allegheny River, 100% of the samples exceeded the PA phenolics standard both upstream and downstream, even though there are no coke plants or blast furnace operations along that river. The median concentration and the mass loading, in pounds per day, of phenolics were higher at the lowest downstream location on the Allegheny than on the Monongahela.

The total cyanide for all the locations on the Ohio River exceeded the PA standard 2% of the time. All the median values were bdl. The median value of free cyanide at each location on the Monongahela and Ohio Rivers was below the detection limit. Free cyanide was not determined for the Allegheny.

TABLE 1

POLLUTANTS
OHIO RIVER BASIN

% Of Reported Values Greater Than PA W.Q. Stds.

	Monongahela R.		Allegheny R.			Ohio R.
	Upstream	Downstream	Upstream	Upstream	Downstream	Downstream
	Charleroi	Smithfield	Freeport	Leechburg	Tarentum	E. Liverpool
Phenolics	31	12	100	100	100	0
Free Cyanide	*	20	---	---	---	*
Total Cyanide**	15	4	0	0	0	0
Zinc	77	25	0	83	0	16
Nickel	0	0	0	67	0	0

* All values were reported at bdl values which were higher than the PA std.
** Std. applies to Ohio River only, other locations are noted for reference.

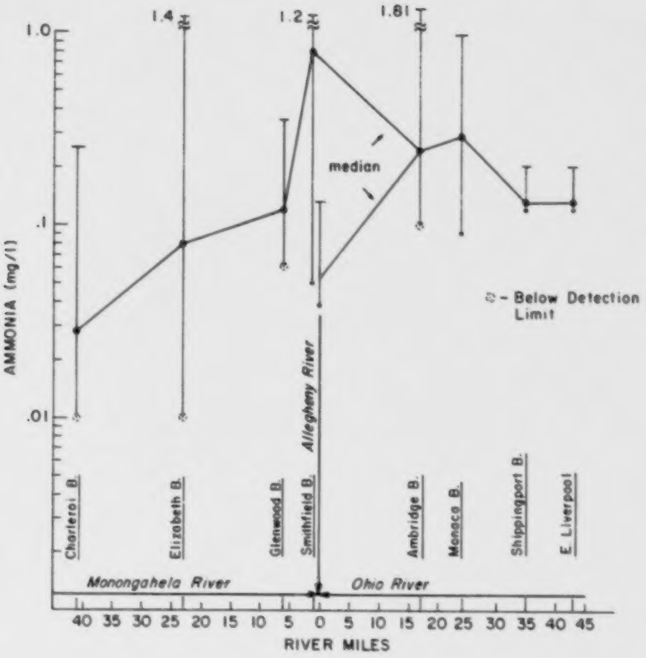


FIGURE 4 Ammonia, Ohio River Basin

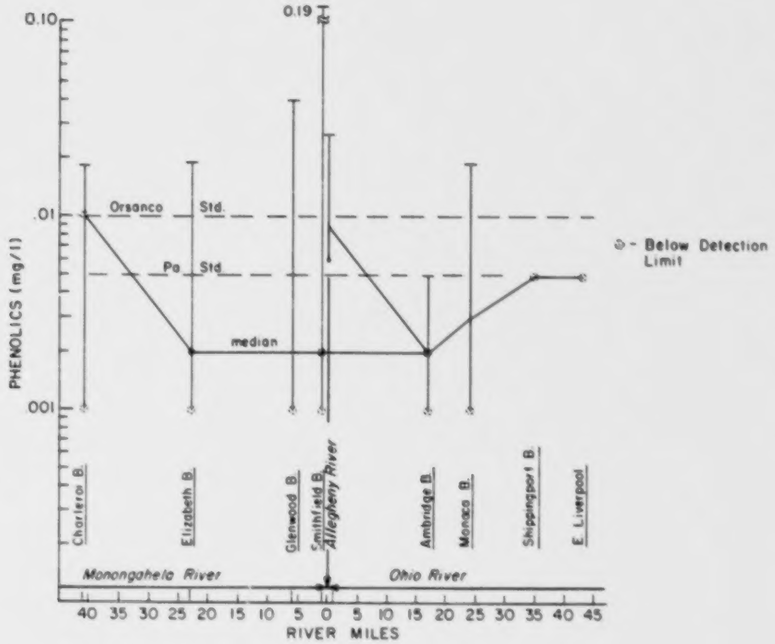


FIGURE 5 Phenolics, Ohio River Basin

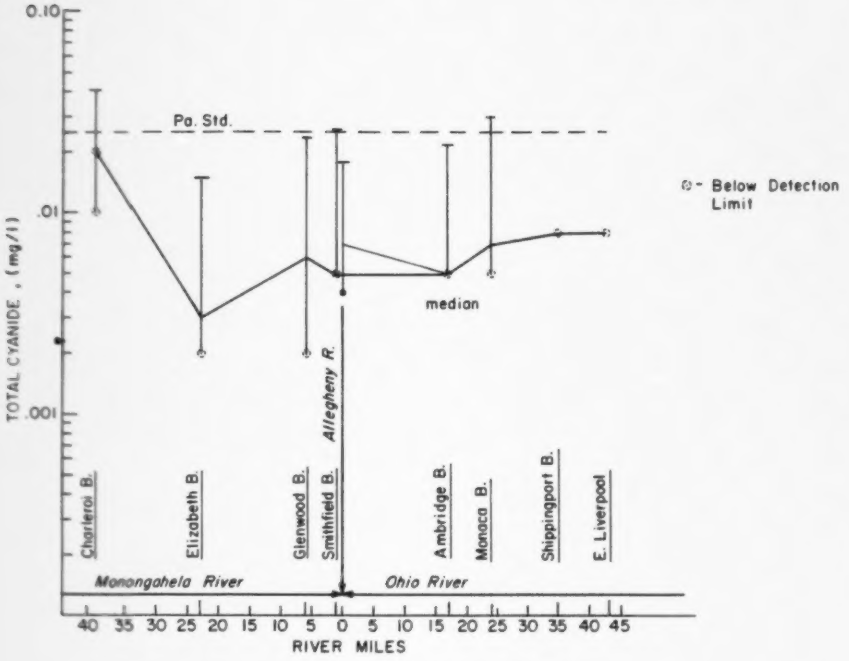


FIGURE 6 Total Cyanide , Ohio River Basin

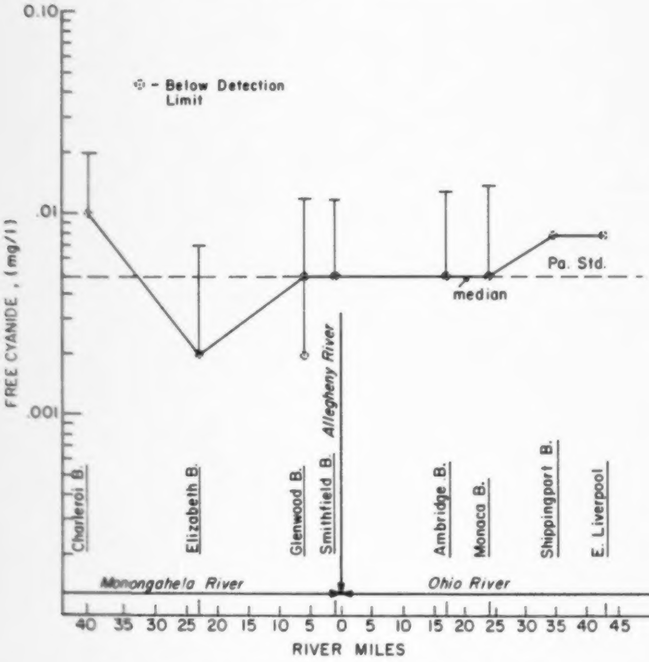


FIGURE 7 Free Cyanide , Ohio River Basin

Smithfield Bridge samples reflect the naturally integrated effect of all the variables of the Monongahela River including wide independent variations in river flow rate, river temperature, coke production, and hot metal production. Linear correlation coefficients were derived for these variables with concentrations of ammonia, total cyanide, free cyanide, and phenolics. These coefficients are listed in Table 2(A). Within the range of values obtained in this study, phenolics concentrations appear to be independent of flow, have weak negative correlation with temperature, and weak positive correlation with coal coked and with hot metal produced. Free cyanide was independent of and total cyanides and low correlation with coke and hot metal production. The weak correlations may be attributable to the narrow ranges and very low concentrations at or near bdl levels of the pollutants. Phenolics concentrations at Smithfield are plotted against river temperature in Figure 8, river flow in Figure 9, and with production data in Figure 10. The analytical data for Smithfield Bridge are summarized in Table 3, and are typical of the data obtained at the other locations.

Correlation coefficients were also determined for phenol versus flow and temperature at Tarentum, the location furthest downstream on the Allegheny. Here the phenol concentration had a low positive correlation with flow, and weak negative correlation with temperature. These are listed in Table 2(B).

LOWER CUYAHOGA BASIN

The average concentrations of pollutants in the lower Cuyahoga are listed below:

	Upstream	Downstream
Ammonia mg/l	2.52	3.58
Free Cyanide mg/l	.016	.031
Total Cyanide mg/l	.036	.057
Phenolics mg/l	.010*	.014
Cadmium mg/l	.012	.012
Chromium mg/l	.016	.017
Copper mg/l	.055	.060
Lead mg/l	.042	.043
Nickel mg/l	.053	.052
Zinc mg/l	.227	.244

*Does not include unexplained high value 1.56 mg/l.

Pollutant concentrations higher than Warmwater Habitat standards were found both upstream and downstream of the steel plants. This is a consequence of this relatively low flow river receiving a high volume of discharges from municipal treatment plants, other industries, and non-point sources, as well as from the steel industry. Correlation coefficients were derived for the concentration of pollutants downstream with flow, temperature and production. These are listed in Table 4. No high correlations were found between the pollutants and the other variables. Phenolics concentrations downstream are plotted with coal and hot metal production in Figure 11.

TABLE 2

CORRELATION COEFFICIENTS

(A) Smithfield Bridge, Monongahela River, Downstream

	Flow cfs	Temp. °F	Ammonia mg/l	Total Cyanide mg/l	Free Cyanide mg/l	Phenolics mg/l	Zinc mg/l	Coal tons/day
Temp.	-.605							
Ammonia	.115	-.318						
Total Cyanide	.066	-.194	-.231					
Free Cyanide	.614	-.545	.254	.240				
Phenolics	-.058	-.417	.498	-.026	.164			
Zinc	.557	-.490	-.188	.290	.339	.010		
Coal	.669	-.704	.472	-.028	.664	.469	.221	
Hot Metal	.529	-.584	.499	-.069	.546	.547	.251	.926

(B) Tarentum, Allegheny River, Downstream

	Phenolics mg/l	Flow cfs
Flow	0.372	
Temp. °F	-.439	-.618

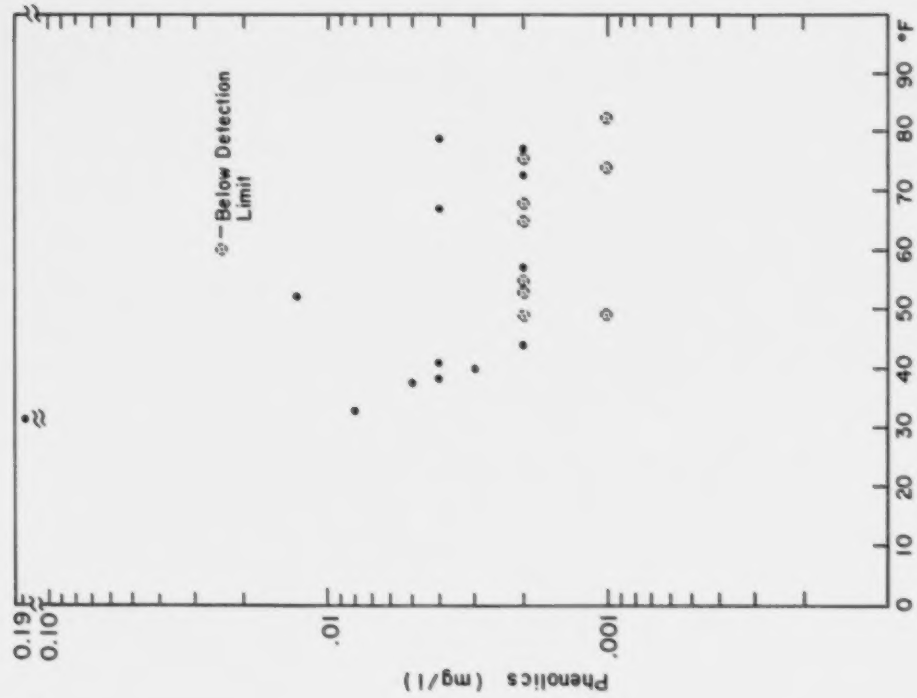


FIGURE 8 Phenolics vs. Temperature , Smithfield

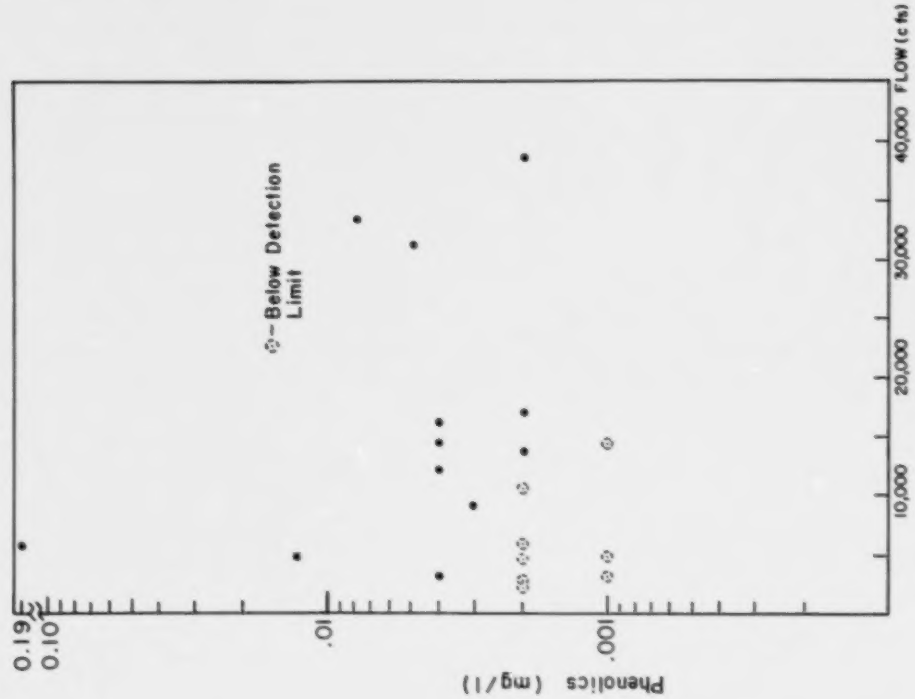


FIGURE 9 Phenolics vs River Flow, Smithfield

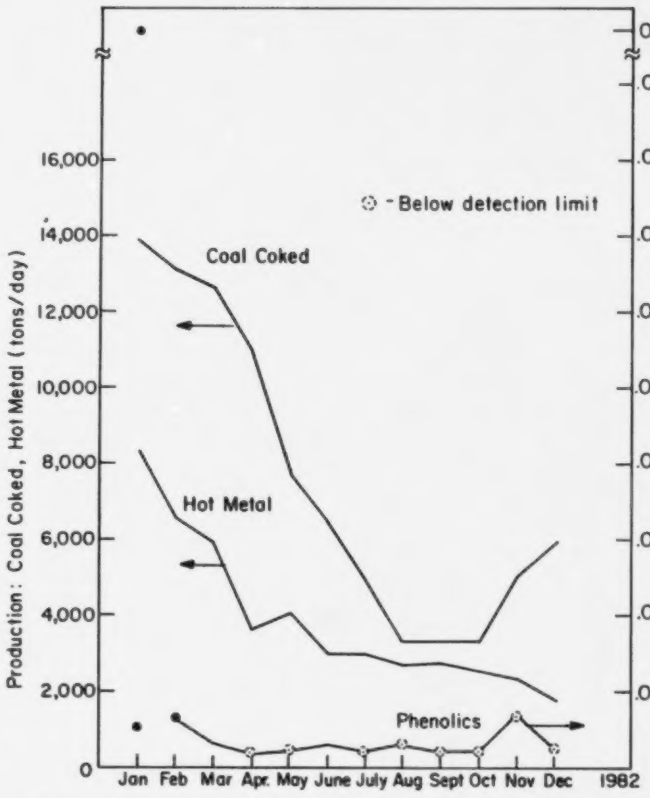


FIGURE 10 Phenolics and Plant Production, Monongahela River downstream.

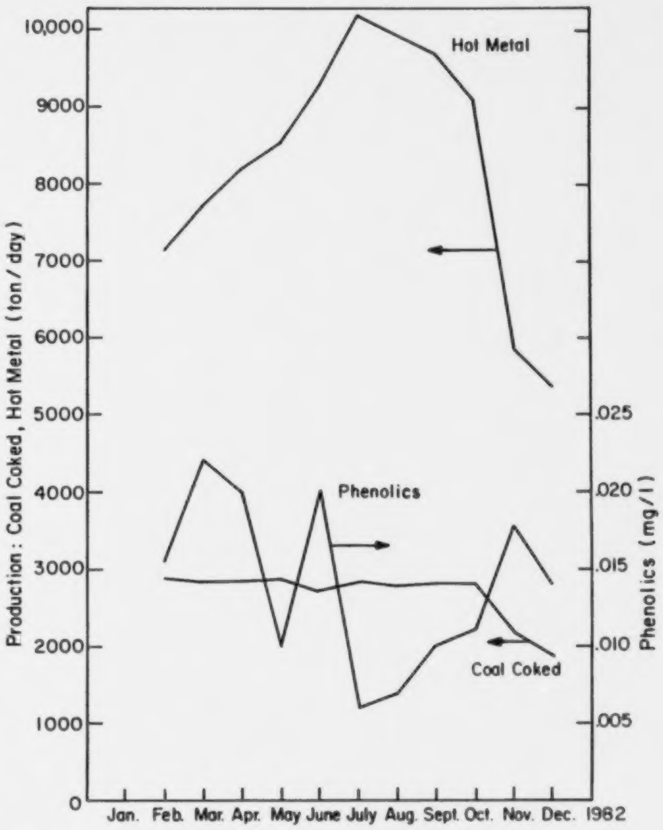


FIGURE 11 Phenolics and Plant Production, Cuyahoga River downstream.

TABLE 3

River: Monongahela
Location: Smithfield Bridge
River Miles: 1

26 samples taken between 1/4/82 and 12/22/82

Item	N	N<	Maximum	Minimum	Avg.1	Avg.2	Median	PA Std.	Mass 1* (lbs/day)	Mass 2* (lbs/day)
River Flowrate(cfs):	26	0	38500.	2150.	10315.	10315.	4960.			
Temp.(F):	26	0	82.	32.	58.	58.	55.			
pH(S.U.):	26	0	7.7	6.5	7.1	7.1	7.1			
Hardness(mg/1):	20	0	174.	71.	114.	114.	110.			
Tot. Sus. Solids(mg/1)	25	0	133.	3.	24.	24.	11.		1347142.	1347142.
Ammonia(mg/1):	21	5	1.200	0.050	0.308	0.284	0.180		17122.	15773.
Free Cyanide(mg/1):	25	18	0.012	< 0.005	0.006	0.002	< 0.005	.005	307.	107.
Total Cyanide(mg/1):	25	11	0.027	< 0.005	0.008	0.006	< 0.005		453.	331.
Phenols(mg/1):	26	13	0.190	< 0.001	0.010	0.009	< 0.002	.005	569.	519.
Cadmium(mg/1)	9	9	< 0.010	< 0.005	< 0.006	0.000	< 0.005	.010	< 340.	0.
Chromium(mg/1):	20	19	0.010	< 0.010	0.010	0.001	< 0.010		556.	28.
Copper(mg/1):	9	9	< 0.010	< 0.010	< 0.010	0.000	< 0.010	.050(C)	< 556.	0.
Iron(mg/1):	20	0	3.370	0.170	1.052	1.052	0.500		58493.	58493.
Lead(mg/1):	20	17	< 0.030	< 0.003	0.016	0.001	0.008	.050	892.	75.
Nickel(mg/1):	20	20	< 0.030	< 0.030	< 0.030	0.000	< 0.030	.050(C)	< 1667.	0.
Selenium(mg/1):	9	8	0.003	< 0.002	0.002	0.000	< 0.002	.010	117.	19.
Zinc(mg/1):	20	5	0.070	< 0.010	0.032	0.029	0.030	.050(C)	1751.	1612.

NOTES:
River Miles are from the Point in Pittsburgh.
N = Number of reported values.
N< = Number of values reported below detection limit.
Avg.1 = Arithmetic average concentration calculated to 3 decimals: N< values assumed = to detection limit.
Avg.2 = Arithmetic average concentration calculated to 3 decimals: N< values assemed = to zero.
(C) = Calculated from 96-hr. LC50.
Mass 1* = Avg.1 x Flowrate.
Mass 2* = Avg.2 x Flowrate.

TABLE 4

CORRELATION COEFFICIENTS

Cuyahoga River, Downstream

	Flow cfs	Temp. °F	Ammonia mg/l	Free Cyanide mg/l	Total Cyanide mg/l	Phenolics mg/l	Zinc mg/l	Coal tons/day
Temp.	-.831							
Ammonia	-.545	.386						
Free Cyanide	-.251	-.027	.335					
Total Cyanide	-.536	.291	.256	.688				
Phenolics	.256	-.509	-.133	.157	-.074			
Zinc	-.282	.257	.645	.158	.205	-.216		
Coal	-.025	.206	.138	.190	.291	-.112	.278	
Hot Metal	-.516	.753	.159	.022	.339	-.360	.248	.710

POINT AND NON-POINT SOURCE CONTROL

Section 305(b) of P.L. 92-500 (Federal Water Pollution Control Act) requires the states to report on their assessment of water quality. The Pennsylvania 1982, 305(b) report declares that for the years 1975 through 1982 Pennsylvania streams exhibited a significant quality improvement trend as programs were initiated to provide, upgrade, and expand facilities for point source discharges. Pennsylvania DER predicts that approximately 82% of the state's major streams will meet fishable, swimmable standards by 1983. However, the report further states, on page 44, that "non-point source pollution continues to constitute the single most serious and widespread water quality problem in the state." Other widespread exceedances of standards arise from agricultural and urban runoff in the drainage basins of the rivers studied. As early as 1962, studies indicated that a significant portion of phenolics in the Monongahela River resulted from decay of natural vegetation.(2) It appears from current data that this is still a major contributor to the exceedances of water quality standards for phenolics. Efforts to mitigate the problems arising from non-point sources have been limited. Assuming that all point (industrial and municipal) discharges will conform to effluent standards, the chronic and pervasive nature of non-point sources will prevent full attainment of water quality goals.

The Ohio EPA reports that the discharge of pollutants from non-point sources has long been recognized as having a major impact on water quality in many of Ohio's major river basins. However, due to the difficulties in initiating control procedures, compared to point source pollution control, many aspects of non-point source pollution management have been severely neglected. Non-point loadings from urban runoff and combined sewer overflows and municipal wastewater treatment plants contribute to the unique water quality characteristics of the lower Cuyahoga.

SUMMARY AND CONCLUSIONS

A data base on concentrations of chosen regulated pollutants was begun for rivers in the upper Ohio River Basin and the lower Cuyahoga River.

In the Ohio River Basin, the maximum concentrations of free cyanide, total cyanide, phenolics, nickel, and zinc occasionally exceeded Pennsylvania water quality standards. However, high values occurred frequently upstream, as well as downstream of the steel plants. Weak correlations were found between phenolics concentration versus temperature and coal and hot metal production downstream on the Monongahela River. High concentrations of phenolics upstream of the steel plants and a very weak correlation of flow with phenolics concentrations lends support to earlier conclusions that much of the phenolics load in the rivers studied are the result of vegetative decay. Most of the metallics were found to be near or below the detection limits, and their analysis was discontinued part way through the project.

The lower Cuyahoga River exhibits a unique water quality situation resulting from its relatively low flow combined with discharges from a large municipal water treatment plant and other industry and non-point sources in addition to the steel industry.

ACKNOWLEDGEMENTS

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(2) R. D. Hoak, "Recovery and Identification of Organics in Water," Int. J. Air Wat. Poll., 1962, Vol. 6, 521-538.

TOXICITY TREATABILITY FOR IRON AND STEELMAKING WASTEWATERS

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ABSTRACT

As part of its toxic pollutant control program, the Environmental Protection Agency (EPA) has gathered some information about certain priority toxic pollutants in wastewaters discharged by the iron and steel industry (46 FR 1858). Little, if any, information is available, however, on the effects of these toxic pollutants and their various combinations on the bioassay (toxicity) test species. Nor is it known how effective the unit treatment processes identified in model treatment and standards systems may be in reducing the concentrations and the toxic effects of these pollutants.

This study developed a methodology to assess the toxicity treatability of the wastewaters from steelmaking and assessed treatment systems in use in eight subcategories. The study was limited to those systems considered assessable under the somewhat low production levels of the study period.

Sampling and analysis programs were conducted utilizing prescribed procedures for conventional water contaminants, toxic organics, and static bioassay. Samples were collected before and after each unit process in the wastewater treatment system. All testing was done under a thorough quality-assurance plan. In this snap-shot approach, all efforts were made to ensure

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(*) PEDCo Environmental, Inc., 11499 Chester Rd., Cincinnati, OH 45246.

representativeness of the samples. For example, if the production facility were operating only one turn, samples were collected only during the operating turn.

The results show the relative toxicity and variability of wastewaters from the different manufacturing subcategories, the treatment effectiveness, and reductions in toxicity.

The relationship between chemical contaminant content and toxicity is examined to the extent possible and with cognizance of the possible site uniqueness of the data.

This paper has been reviewed in accordance with the U.S. Environmental Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

As part of the toxic pollutant control program, the U.S. Environmental Protection Agency is developing industry specific toxicity data. The Agency has gathered information relevant to specific priority toxic pollutants discharged by the iron and steel industry (46 FR 1858). Minimal information is available, however, on the effects of these toxic pollutants, and their various combinations, on the bioassay (toxicity) test species.

Because a bioassay can simultaneously assess the effects of numerous toxic pollutants, it is a useful test of overall toxicity, and of toxicity reduction resulting from various wastewater treatments. Bioassay data, together with toxic pollutant data and the relevant parameters of the industrial process, can guide the formulation of regulatory strategy and help in the selection of effective treatments that will reduce toxic impacts on receiving waters.

This study develops data on toxicity and toxicity variability for wastewaters generated in selected iron and steelmaking processes, assesses the effectiveness of the treatments in reducing both toxic pollutants as determined by chemical analysis, and total toxicity as measured by bioassay. The study was limited to those systems considered assessable under the somewhat low production levels of the study period.

The wastewater data are examined for possible relationships between chemical contaminant content and static bioassay toxicity, and for correspondence between chemical contaminant reduction and toxicity reduction.

LITERATURE REVIEW

Raw wastewaters from iron and steel manufacturing have been characterized chemically using historical data from a broad range of manufacturers (Development Document, 1982). Pollutant concentrations, based on loadings for model plants, were developed for process subcategories. These are summarized in Table 1 for the eight subcategories chosen for biotoxicity evaluation: cokemaking, ironmaking, steelmaking, continuous casting, hot forming, pickling, cold forming, and hot coating. Most of the toxic pollutants are found in cokemaking and cold forming; although, as shown, potentially toxic pollutants are present in all eight wastewaters.

All these model processes except cold forming include some recycling of wastewaters. Water recycle, while reducing overall discharge, would be expected by itself to concentrate wastewaters and increase toxicity. Control

TABLE 1. IRON AND STEEL MAKING RAW WASTEWATER CHARACTERISTICS[a,b]

Characteristics	Coke-making	Iron-making	Steelmaking[c]		Contin. Cast.	Hot Forming	Pickling			Cold Forming			Hot Coating	
			S.C.	W.O.			H_2SO_4	HCl	Comb.	Comb.	Recirc.	Once Thru	Galv.	Terne
Flow, l/kkg	676	13353	4172	4590	14188	14188	864	693[d]	963[d]	1252	104	1669	10013	2503
pH, SU	7-10	6-9	7-12	8-11	6-9	<1-6.4	<1-6.4	<1-5	4-8.2	6-9	6-9	6-9	3-9	2-8
Ammonia-N	600	20												
Oil and grease	75				25	56	11	10	10	1481	14700	1215	25	30
Phenolics (4-AAP)	300	3												
Sulfide	150													
Dissolved iron							2800	1200	740					
Thiocyanate	480													
Residual Chlorine														
Total susp. solids	50	1900	720	4200	60	3000	120	30	49	843	1013	135	80	75
Fluorides		15	15	20					1200					
1 Acenaphthene											0.055			
3 Acrylonitrile	1.2													
4 Benzene	3.5[e]													
6 Carbon tetrachloride												0.007		
9 Hexachlorobenzene	0.01													
11 1,1,1-Trichloroethane												0.043		
13 1,1-Dichloroethane														
21 2,4,6-Trichlorophenol	0.1													
22 Parachlorometacresol	0.6													
23 Chloroform	0.3[e]			0.05							0.037			
31 2,4-Dichlorophenol	0.01													
34 2,4 Dimethylphenol	5	0.05												
35 2,4 Dinitrotoluene	0.2													
36 2,6 Dinitrotoluene	0.1													
38 Ethylbenzene	3													
39 Fluoranthene	0.8[e]	0.08								0.071	0.27			
54 Isophorone	0.5													
55 Naphthalene	30[e]									4	1.5	4.4		
60 4,6-Dinitro-o-cresol	0.12										0.063			
64 Pentachlorophenol	0.12													
65 Phenol	275[e]	0.65[e]									0.17			
66-71 Total phthalates	5													

See footnotes at end of table.

(continued)

TABLE 1 (continued)

Characteristics	Coke-making	Iron-making	Steelmaking[c]		Contin. Cast.	Hot Forming	Pickling			Cold Forming			Hot Coating	
			S.C.	W.O.			H_2SO_4	HCl	Comb.	Comb.	Recirc.	Once Thru	Galv.	Terne
72 Benzo(a) anthracene	0.3										0.16			
73 Benzo(a)pyrene	0.1[e]	0.01												
76 Chrysene	0.4[e]	0.01									0.11			
77 Acenaphthylene	3.5[e]										0.14			
78 Anthracene										0.18	0.14	0.014		
80 Fluorene	0.6[e]									0.98	3.5			
81 Phenanthrene										5.1	0.91			
84 Pyrene	0.6[e]	0.05[e]								0.05	0.3			
85 Tetrachloroethylene										0.02	0.036	0.02		
86 Toluene	25[e]										0.012	0.69		
87 Trichloroethylene											0.009			
114 Antimony	0.2[e]	0.04						0.54[e]	0.38[e]		0.031			
115 Arsenic	2[e]	0.1[e]		0.06[e]			0.17[e]	0.11[e]		0.16[e]	0.26[e]	0.02	0.25	0.15
117 Beryllium												0.01		
118 Cadmium		0.1[e]	0.06	0.4			0.02	0.01	0.01		0.11[e]			0.3[e]
119 Chromium		0.5	0.6		0.65	1.3	6.9[e]	1.0[e]	76[e]	0.03[e]	2.5[e]	0.04	2[e]	5[e]
120 Copper		0.25[e]	0.15[e]	5.2[e]	0.11	5.7	1.3[e]	0.72[e]	3.8[e]	0.89[e]	7.1[e]	0.17[e]	0.08[e]	0.6
121 Cyanide	50[e]	12[e]												
122 Lead		5	8	3.9[e]	0.08	6.5	0.2[e]	2.6[e]	0.05	0.1	2.9[e]	0.39	2[e]	1.2[e]
123 Mercury				0.02										
124 Nickel		0.1[e]	0.3[e]	0.4		5.7	2.4[e]	1.5[e]	95[e]	0.21[e]	3.3[e]	0.2[e]	0.5[e]	1[e]
125 Selenium	0.2[e]	0.06		0.02	0.08									
126 Silver			0.02	0.08			0.02							
127 Thallium				0.03										
128 Zinc	0.2[e]	20[e]	6.8[e]	14[e]	0.7	3.1	5.6	7[e]	0.64	0.15[e]	3.7[e]	0.098	1.0[e]	1.5[e]
130 Xylene	12[e]													3
Tin														

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[a] From Development Document for Effluent Limitation Guidelines and Standards, (EPA-440/1-82-024)

[b] All concentrations are in mg/ℓ unless otherwise noted.

[c] S.C. = suppressed combustion W.O. = wet open combustion

[d] Flow in L/min

[e] Pollutant found in all samples

TABLE 2. REGULATED POLLUTANT LIST, IRON AND STEEL INDUSTRY

4	Benzene
55	Naphthalene
73	Benzo(a)pyrene
85	Tetrachloroethylene
119	Chromium
121	Cyanide
122	Lead
124	Nickel
128	Zinc
	Ammonia
	Oil and Grease
	pH
	Phenol (4-AAP)
	Residual Chlorine
	Total Suspended Solids
	Hexavalent Chromium

Source: Development Document for Effluent Limitation Guidelines and Standards, Iron and Steel Manufacturing (EPA-440/1-82-024).

of regulated pollutants listed in Table 2, and other toxic pollutants known to be present, has been assessed for these subcategories, in each of which treatment technologies have been examined as to their demonstration status, application, and performance in reducing pollutant concentration. This assessment does not include effectiveness in reducing biotoxicity; hence, there is no basis for relating the reductions in toxic chemical content to reductions in biotoxicity. The information gained, however, provides the basis for selection of subcategories for biotoxicity assessment.

The effectiveness of wastewater treatment technologies in reducing biotoxicity is not inherent in outfall compliance data. Outfalls represent the results of accumulative treatment and collection. These data nevertheless do identify toxicities that persist after currently applied treatments. Therefore, available bioassay test results were summarized (Table 3) to guide the selection of systems for further study. Table 3 indicates the treatment technologies applied, the number of plants tested, the year of test, and the LC_{50} or range thereof. The treatments are indicated by symbols which are defined in Table 4. The data began in 1975, but most of the data are more recent. Fathead minnows and daphnia were the most commonly used test organisms, but bluegills and shrimp were also used, as indicated. Both static and flow-through tests are included.

Persistent toxicity is evident in outfalls from cokemaking and ironmaking. Cold forming effluents tested do not show much toxicity; the treatments need investigation to determine their effectiveness and the loadings involved. No data are available for Hot Coating and Continuous Casting. Three combined effluents showed an LC_{50} range from 19.5 percent to no mortality (NM).

TABLE 3. BIOASSAYS OF IRON AND STEEL EFFLUENTS

Subcategory	Wastewater treatments[a]	Number of plants tested	Test Year	LC_{50}, % Fathead Minnow	LC_{50}, % Daphnia Pulex (Magna)	Reference
Cokemaking	BOA1, SL	1	81	15% mortality	24 (bluegill)	2, 3
	ASF, BOA1	3	81	<10 - 44	14.5 - NM[b]	2, 3
	ASF, DP, BOA1	2	80/81	15-65% mortality	Med. toxic	4
	ASF, DP, BOA1, CA	1	80	20-100% mortality	-	5
Ironmaking	T, VF, FLP, CT, FP	1	79/80		(82 - NM)	6
	CL, T, VF, FLP	1	81/78	<43-10% mortality	(<6 - NM)	7,8
	CL, FLL, CLB, FDSG, CA	1	78	5% mortality (bluegill)		9
	SL, PSP, SS, FLF, FLL, CL, FLP	1	80		(NM)	10
Steelmaking	CL, FLP, SL	1	79		(NM)	11
	SSP, CT, FDSP, SS	1	78		(20% mort - NM) (Shrimp)	12
	AO, FLF, A, CL	1	80/81		(NM)	13,14
Hot forming	PSP, FDO, CL, SS, NC, SL	1	79		(NM)	11
	FLP, SB, SS	1	79		(NM)	15
	SB, SL, SS, FLP	1	80		(10% mort)	16
Pickling	NC, SL	1	78		(NM)	17
	PSP, FDO, CL, SS, NC, SL	1	79		(NM)	11
	AO, FLF, A, CL	1	80/81		(NM)	13,14
Cold forming	NC, SL	1	78		(NM)	17
	None	1	80		NM but organism floated	6
				on surface		
	AO, FLF, A, CL	1	79		(10% mort)	15
		80		(NM)	(NM)	13,14
Hot coating	No data available					
Continuous casting	No data available					
Combined effluent	Various	3	75/80/81	NM	(19.5 - NM)	2, 10, 18

[a] Abbreviations defined in Table 4.

[b] NM = no mortality.

TABLE 4. List of Abbreviations for Wastewater Treatments

A	acidification
AF	air flotation
AO	air oxidation
ASF	free ammonia still
ASFF	free and fixed ammonia still
ASFF-L	free and fixed ammonia still-lime addition
BOA-1	one-stage biological reactor
BOA-2	two-stage biological reactor
CA	carbon adsorption
CAG	carbon adsorption, granular
CL	clarifier
CLA	alkaline chlorination
CLB	break point chlorination
CNT	central treatment
CPT	chrome pretreatment
CT	cooling tower
CYPT	cyanide pretreatment
DP	dephenolization
DS	desulfurization
E	equalization
FDMMG	deep filtration, mixed media, gravity
FDMMP	deep filtration, mixed media, pressure
FDO	deep filter with walnut shells
FDS	deep sand filter
FDSP	deep sand filter, pressure
FDW	deep walnut shell filter
FM-A	flash mixture - alum.
FLA	flocculation with alum
FLF	flocculation with ferric chloride
FLL	flocculation with lime
FLP	flocculation with polymer
FP	pressure filtration
N	neutralization
NA	neutralization with acid
NC	neutralization with caustic
NL	neutralization with lime
PSP	primary scale pit
RC( )	recycle (percent)
SB	settling basin
SL	settling lagoon
SL-U	settling lagoon for underflow
ST-CL	scalping tank with chlorination
SS	surface skimmer
SSP	secondary scale pit
T	thickener
VF	vacuum filtration
VF-S	vacuum filtration of sludge

Since existing data on chemical toxicity do not also show biotoxicity, and vice versa, these data provide us no basis for relating the reductions in toxic chemical content to reductions in biotoxicity. The data do, however, provide a basis for selecting of treatment technologies for further study.

SELECTION OF TREATMENT SYSTEMS FOR STUDY

For the eight steelmaking subcategories identified in Table 1, and for the quite-commonly practiced central treatment, plant wastewater treatment systems were selected for further study. Criteria applied in the selection included:

> anticipated difficulties in treatment, with potential for treatment problems;
>
> applied technologies representative of BPT, BAT, or NSPS systems*; and
>
> combined wastewaters sent to central treatment likely to present problems.

Using these criteria, treatment technologies were selected and tested in seven different plants. Table 5 shows the treatment technologies tested. Some plants with representative technologies were not involved in the study because their production facilities were operating at lower levels than normal. Thus, the two-stage biological reactor system for cokemaking wastewaters was not studied, although it is the BAT technology, because none were operating as such at the time. One selected system could have operated as BOA-2.

Wastewater treatment plants in the U.S. steel plants are each somewhat unique, and indeed different both from each other and from the BPT and BAT model plants. While the selected treatment systems offer many of the unit processes inherent in BPT and BAT, a complete match, process by process, seldom exists. The systems selected do include those unit processes which have been shown to effect decreases in pollutant loadings, and might therefore effect decreases in toxicity.

One of the selected treatment systems for ironmaking represents BAT-4 technology, except for lack of dechlorination, final filtering, and discharge. The steelmaking treatment system for suppressed combustion was operating essentially as a BPT system with 100 percent recycle. The semi-wet system was BAT, except for moderate blowdown.

One continuous casting system is BPT with the addition of total recycle. The other has blowdown from the scale-pit to a municipal sewer.

The hot strip mill treatment system at plant A does not include the filtration step of BPT. However, alternatives are used, including flocculation with polymer and with alum, and central treatment along with combined

---

(*) Best practicable technology, best available technology, and new source performance standards.

TABLE 5. WASTEWATER TREATMENTS SELECTED FOR STUDY

Subcategory	Treatments[a] (as designated in EPA-440/1-82-024)	Plant
Cokemaking	ASFF; DS; CT; Dilution; BOA-1; CL	C
	ASFF; BOA-1; T	D
	ASFF; DS; E; CL; FDMMP; CAG; CLA	G
	↑[b]	
Ironmaking	PSP; FLP; T; CT; RC(96) → CL; CLA → Quench	A
	PSP; FLP; T	D
Steelmaking		
Suppressed Combustion	FLP; T; RC → CL	A
Semi-Wet Open	FLP; T; A; RC →	A
Continuous Casting	PSP; SS; FDW; CT; RC	B
	(FDW: backwash to slab mill system)	
	PSP; SS; FDS; RC	E
	↓	
Hot Forming		
Hot strip mill	PSP; SS; FLP (cold rolling wastewater); FLA; CL; SS; ST-CL (other wastewater); CT; SB; RC	A
	PSP; SS; FDMMG	D
	PSP; SB; SS; FDSP	F
Slabbing mill	PSP; → Hot strip mill system	A
	PSP; E; FLP; SS	B
Bar mill	PSP; FLP; FLA; FLL; A; CL; CT; RC	A
Section mill	PSP; SS; CNT	E
Pickling, comb	E; NL; CL	F
HCl	Rinse and fume scrubber to SS; cold forming treatment system	B
Cold Forming	PSP; SS; Hot Forming System at FLP	A
Recycle	SB; SS; CNT	A
Once through	SS (pickling wastewater); SL; AO; NL; FLP; CL (Discharge); T	B
	VF	
Hot Coating	↑	
Galvanizing	E; NL; FLP; CL	C
Central Treatment	ST-CL; CT; SB; RC	A
	CPT; CYPT; NC-NA; FLP; CL; SS	E

[a] Abbreviations defined in Table 4.

[b] Arrows indicate withdrawal of a sludge.

wastewaters. Usually, the treated waters are recycled without blowdown. Plant D processes hot strip mill wastewater along with slabbling mill wastewaters, using filtration prior to direct discharge. Plant F uses settling tanks for clarification, thus closely approximating BPT, and then filters the waters from hot-strip, universal, and blowing mills. The treated waters are directly discharged.

Slabbing mill wastewaters at plant A are combined with hot-strip mill waters for treatment. Plant B uses polymer treatment and oil skimming in an equalization basin before directly discharging the treated water.

The bar-mill treatment system does not include filtration, but adds flocculation and clarification, and then recycles as does BAT-1.

The section mill wastewaters, Plant E, are given settling basin and oil skimming treatments, then sent to a central treating system for equalization, neutralization, and flocculation with polymers before discharge.

Plant F uses a BPT treatment system, except for air flotation. Plant B passes pretreated wastewater to the cold-forming wastewater treatment system where treatment somewhat better than BPT BAT-1 is carried out.

Plant A recycles cold rolling mill wastewaters after treating them combined with hot strip mill waters. Its tandem mill wastewater is pumped to a central treatment system on a once-through basis. Plant B uses a system equivalent to BPT.

The hot coating treatment system resembles BPT without chrome reductions.

Two different central treatment systems were studied. One involved settling with chlorination and recycle. The other received a more varied loading, requiring pretreatment for cyanide and chrome, followed by neutralization, flocculation with polymer, and clarification with skimming before direct discharge.

SAMPLING AND ANALYSIS

Both sampling and analysis were conducted using approved techniques (19, 20, 21). Sampling sites were selected upstream and downstream of treatment unit processes. Composite samples were obtained using Isco Model 2100 automatic samplers at all locations except those in designated hazardous areas. Composites in such areas were made from a corresponding set of grab samples. Sampling periods for compositing were coordinated with production schedules. Thus where 24-hour operation occurred -- as in cokemaking, ironmaking, and steelmaking -- sampling continued over that period. Where operation was limited in the number of turns (shifts) per week -- as in many finishing operations -- the sampling was similarly limited to avoid collection of wastewaters which were not receiving raw loadings from the production lines. Composite sample increments were taken automatically every 15/30 minutes depending on the length of the sampling period, or by hand every 3 or 4 hours.

To prevent losses of cyanide, volatile organics, and oil and grease through sample degradation that might occur during composite sampling, grab samples were taken for these constituents. Grab samples were also taken for on-site determination of pH, dissolved oxygen, and residual chlorine. Sample containers were packed in coolers with ice. Bioassay samples were delivered immediately by the fastest possible means to EPA testing laboratories. Chemical analysis samples, preserved with ice, were transported under a chain of custody, and were analyzed within the prescribed limited holding periods (20).

Table 6 identifies the methods of chemical analysis employed (19, 20, 21). Test detection limits, standard deviations, and percent recovery are indicated. These values are given in the recommendations for the methods. During this study, 10 percent of the composite samples taken were split for chemical analysis by both laboratories for quality control purposes. The volatile organics and extractable organics analyses (methods 624 and 625) yielded spectra which were screened for toxic and priority organics, pesticides, and PCB's, generally at detection limits below 10 micrograms per liter.

RESULTS

Analytical results indicate that in general the wastewaters sampled are representative of their respective subcategories. While some raw wastewater values are markedly different from median values developed by the Agency in its industry profiles, the overall characterization shows typical subcategory trends. Results presented here of course represent only one 24-hour period, while subcategory data represent years of operation.

The analyses of raw waste waters, intermediate samples, and samples after final treatment are given in Tables 7 through 26. The percent reductions of pollutants are also shown. Toxicity reductions are not treated in this manner, since an increase in LC_{50}, the reported toxicity rating, denotes a reduction in toxicity. The tabulated results are limited to the regulated pollutants. However, total organics data were compiled as the sum of all identified priority toxic pollutants, and these totals are also shown. Similarly, for metals, the totals are given. Comparisons among the systems tested lead to the following conclusions.

COKEMAKING

The physical/chemical system effluent showed by far the lowest toxicity. It also showed the lowest total organics, metals, and ammonia. Residual toxicity in this system may be due to its high cyanide concentration. Single stage biosystems effluents were very toxic. They differed significantly in concentrations of cyanide, ammonia, and total organics. Biotreatment that includes nitrification tends to remove free cyanide efficiently, except for complex metal cyanides. The buildup of metals that so complex across the adsorbers was confirmed by subsequent tests involving three independent laboratories.

TABLE 6. Methods of Analysis

Constituent	Method No.[a]	Recovery (%)	Detection limit (µg/ℓ)	Standard deviation (µg/ℓ)
Antimony	204.2	NA[b]	3	NA
Arsenic	206.2	85-88	1	±9% R[c]
Chromium	218.2	97-102	1	±0.8
Copper[d]	220.2	97	1	±3.8
Iron	236.1	1.8 B[e]	30	±173
Lead	239.2	85.95	1	±3.7
Nickel[d]	249.2	100	1	±10
Selenium	270.2	94-112	2	14% R
Zinc	289.1	56.6 B	.5	18
Total cyanide	335.2	85-102	20	±620
Ammonia	350.2	-5.5 B	50	±122
Fluoride	340.2	--	100	±30
Oil and grease	413.1	93	--	±900
pH	150.1	±0.16 unit	--	±0.12 unit
Phenolics (4AAP)	420.1	--	5	±4.2
Residual chlorine	330.3	--	1 mg/ℓ	±0.09 mg/ℓ
Total suspended solids	160.2	NA	NA	NA
Volatile organics	624	NA	10	NA
Extractable organics (base/neutral and acids)	625	NA	10	NA
Toxicological	--	--	--	--

[a] Reference 21 for toxicological, References 19 and 20 for all others.

[b] NA = not available according to method.

[c] R = Relative standard deviation.

[d] Limits from analyses made during this study.

[e] B = percent bias.

TABLE 7. COKEMAKING: POLLUTANT REDUCTION, PLANT C[a]

Component	Units	ASFF;DS;DP Δ	; Δ	E ; Δ	CT;Dilution:BOA-1;CL Δ	Percent reduction
Flow	m^3/min			0.83	1.1	
pH	S.U.	10	5	9	7.8	
Ammonia	mg/L	1,420	67.5	1,002	612[a]	(39)
Oil and grease	mg/L	14.4	10.85	26.3	6.4	(76)
Phenol (4AAP)	mg/L	1,060	50.8	831	0.23	(99.9)
Residual chlorine	mg/L					
Total suspended solids	mg/L	28	<2	80	216	-
Benzene	µg/L	4.2	58,500	11,600		
Naphthalene	µg/L	-	9,500	783	<2	99.7
Benzo(a)pyrene	µg/L	-	-	ND	136[a]	-
Tetrachloroethylene	µg/L	-	-	-	-	-
Cyanide	mg/L	-	-	<0.02	20.2[a]	-
Total organics	µg/L	-	-	73,233	916	99.9
Lead	µg/L	-	-	-	-	-
Nickel	µg/L					
Zinc	µg/L	1,910	500	650	310[a]	52.3
Total metals	µg/L	4,294	804	2,694	1,679	38
Toxicity, Minnow, 96 hr	LC_{50}	0.61	0.61		3.8	
Daphnia, 48 hr	LC_{50}	0.4	<1.0		1.5	

[a] Treatments shown in Tables 7 - 26 may differ from those shown in Table 5 because of changes made subsequent to issue of the Guidelines document EPA-440/1-82-024.

TABLE 8. COKEMAKING: POLLUTANT REDUCTION, PLANT D

Component	Units	Light Oil + Final Cooler Condensate ASFF-L → ; E; ↓ Δ	BOA-1; T Δ	Percent reduction
Flow	m^3/min	1.0	0.9-1.25	
pH	S.U.	11.9	12.2	
Ammonia	mg/L	107	22.7[a]	78
Oil and grease	mg/L	11.1	14.6	-
Phenol 4(AAP)	mg/L	149	111[a]	25
Residual chlorine	mg/L	-	-	-
Total suspended solids	mg/L	1,040	529	49
Benzene	µg/L	3,570	212	94
Naphthalene	µg/L	4,130	392	90.5
Benzo(a)pyrene	µg/L	<10	<10[a]	-
Tetrachloroethylene	µg/L	-	-	-
Cyanide	mg/L	0.1	0.46	-
Total organics	µg/L	129,867	80,326	38
Lead	µg/L	-	-	-
Nickel	µg/L	-	-	-
Zinc	µg/L	240	110[a]	54
Total metals	µg/L	899	810	9.9
Toxicity, Minnow, 96 hr	LC_{50}	4.42	8.84[a]	-
Daphnia, 48 hr	LC_{50}	1.6	<1.6[b]	-

[a] 32.3 on 3-7, 83 (original test 11-30-82).

[b] 31 on 3-7, 83.

TABLE 9. COKEMAKING: POLLUTANT REDUCTION, PLANT G

Component	Units	HOD; Δ	ASFF;DP; → AF → Δ	E Δ ;	CL Δ ; FDMMP	; Δ	CAG ; CLA		Percent reduction
Flow	m^3/min	0.08	0.08	0.67	0.67	0.67	0.67	0.69	
pH	S.U.	6.8	6.6	8.4	8.4	8.2	8.4	8.8	
Ammonia	mg/L	1.4	1.4	17	16.7 (2)[a]	16.8 (2)	16.8 (2)	ND	99
Oil and grease	mg/L	-	12.6	1.37	28.9 (-2,000)	15.4 (48)	ND (>99)	8.8	70
Phenol (4AAP)	mg/L	87	745	390	601 (-54)	82 (86)	22 (95)	ND	>99
Residual chlorine	mg/L	-	-	-	-	-	-	9.1[c]	-
Total suspended solids	mg/L	21	2	159	107 (33)	33 (79)	5 (97)	16	90
Benzene	μg/L	880	1,200	18,000	15,000 (17)	9,000 (50)	BDL[b]	BDL	100
Naphthalene	μg/L	1,200	720	250	1,700 (-580)	1,100 (35)	BDL (98)	BDL	98
Benzo(a)pyrene	μg/L	-	-	-	-	-	-	-	-
Tetrachloroethylene	mg/L	-	-	-	-	-	-	-	-
Cyanide	mg/L	0.07	0.066	54.2	44.0 (19)	43.3 (20)	31.2 (42)	6.8[c]	(87)
Total organics	μg/L	13,085	13,445	32,333	26,873	19,034	BDL	30	99.9
Lead	μg/L	16.7	2.9	19	16.7 (12)	ND (>99)	9.2 (51)	9.2	51
Nickel	μg/L	ND	ND	35.2	29.2 (17)	13.3 (62)	32.1 (9)	37.2	-6
Zinc	μg/L	39	22	870	107 (87)	72 (92)	15 (98)	17	98
Total metals	μg/L	70.6	27	1,499	591	414	3,800	3,841[c]	-156
Toxicity, Minnow, 96 hr	LC_{50}	12.5	25	0.85	0.72	0.67	1.0	71.5	
Daphnia, 48 hr	EC_{50}	-	50	60% survived in 5%	75% survived in 2%			5.3	
24 hr		2.1				1.3	1.5		

[a] Values in ( ) are cumulative % reduction across the intermediate processes.

[b] <10 μg/L.

TABLE 10. IRONMAKING: POLLUTANT REDUCTION, PLANT A

Component	Units	PSP; Δ	FLP;	T; Δ	CT;	RC(96) →	CL;	CLA → Δ	Quench	Percent reduction
Flow	m^3/min	30.3		30.3				1.1		
pH	S.U.	7.1		7.0				7.6		
Ammonia	mg/L	79		57.8 (27)[a]				<0.4		99.5
Oil and grease	mg/L	9.5		2.7 (71)				5.6		41
Phenol 4(AAP)	mg/L	0.25		<0.06 (76)				<0.06		76
Residual chlorine	mg/L							26.5[b]		
Total suspended solids	mg/L	9,604		29 (99.7)				203		97.9
Benzene	μg/L	ND		ND				ND		--
Naphthalene	μg/L	10		ND				ND		99
Benzo(a)pyrene	μg/L	ND		ND				ND		--
Tetrachloroethylene	μg/L	ND		ND				ND		--
Cyanide	mg/L	b		0.042				<0.02		52.4
Total organics	μg/L	23		ND				ND		99
Lead	μg/L	73,967		533 (99.3)				32.8		99.9
Nickel	μg/L	119		20.5 (83)				<19		84
Zinc	μg/L	349,340		24,790 (93)				4,100[b]		98.8
Total metals	μg/L	427,833		25,384 (94)				4,172		99
Toxicity, Minnow, 96 hr	LC_{50}	21.5		18.4				22.6		
Daphnia, 48 hr	EC_{50}	7.1		5.1				6.8		

[a] Values in parentheses are cumulative percent reduction.

[b] Not quantified due to sample turbidity.

TABLE 11. IRONMAKING: POLLUTANT REDUCTION, PLANT D

Component	Units	PSP	Dekishing water FLP; Δ	T	Percent reduction
Flow	m^3/min	1.7	56.8	56.8	
pH	S.U.	12	7.1	6.9	
Ammonia	mg/L	2.6	5.5[a]	3.6[a]	35
Oil and grease	mg/L	8.2	4.2	2.2	47.6
Phenol 4(AAP)	mg/L	0.09	0.12	0.07	41.7
Residual chlorine	mg/L		<0.02	<0.02	--
Total suspended solids	mg/L	133	847	38	95.5
Benzene	μg/L	ND	ND	ND	
Naphthalene	μg/L	ND	ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	0.05	
Total organics	μg/L	ND	ND	ND	
Lead	μg/L	<1.9	329	61.2	81.4
Nickel	μg/L	174	193	13	93.3
Zinc	μg/L	<30	1,570[a]	300	80.9
Total metals	μg/L	291	2,164	380	82.4
Toxicity, Minnow, 96 hr	LC_{50}		100% survival in 100%	100% survival in 100%	
Daphnia, 48 hr	EC_{50}		55.2	42.1	

TABLE 12. STEELMAKING, SUPPRESSED COMBUSTION: POLLUTANT REDUCTION, PLANT A

Component	Units	Classifier Δ	Secondary vent Δ	Δ	FLP; T; Δ	RC; CL	Percent reduction
Flow	m^3/min	11.4	3.7	15.1	15.1		
pH	S.U.	12.4	--		11.6		
Ammonia	mg/L	1	0.8	0.95	0.4		
Oil and grease	mg/L	10.9	6.5	9.8	5.1		
Phenol 4(AAP)	mg/L	0.52	0.79	0.59	0.6[b]		
Residual chlorine	mg/L	<0.2	--		<0.2		
Total suspended solids	mg/L	9,644	931	7,509	73		
Benzene	μg/L	ND	4.5	1.1	ND		99
Naphthalene	μg/L	ND	4.4	1.07	2		--
Benzo(a)pyrene	μg/L	ND	ND		ND		
Tetrachloroethylene	μg/L	ND	ND		ND		
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02		
Total organics	μg/L	ND	8.9	2.2	2		9
Lead	μg/L	102,000	8,240	79,026	811[b]		99
Nickel	μg/L	4,180	1,280	3,469	6		99.8
Zinc	μg/L	194,000	23,200	152,148	852		99.4
Total metals	μg/L	304,424	33,582	238,059	1,700[b]		99.3
Toxicity, Minnow, 96 hr	LC_{50}		Sample lost lab accident		71		
Daphnia, 48 hr	EC_{50}		Sample lost lab accident		58.6		

[a] Constructed from classifier and secondary vent.

TABLE 13. STEELMAKING: SEMI-WET OPEN, PLANT A

Component	Units	Scrubber surge tank Δ	FLP; Δ	T;	A; Δ	RC	Percent reduction
Flow	m^3/min	--	22.7		22.7		
pH	S.U.	10.3	10.9		9.3		
Ammonia	mg/L	1.7	0.5		0.6		
Oil and grease	mg/L	3.1	3.1		5.6		
Phenol 4(AAP)	mg/L	<0.06	<0.06		<0.06		
Residual chlorine	mg/L	ND	ND		ND		
Total suspended solids	mg/L	1,894	1,302		19.5		98.5
Benzene	μg/L	ND	ND		ND		
Naphthalene	μg/L	ND	ND		ND		
Benzo(a)pyrene	μg/L	ND	ND		ND		
Tetrachloroethylene	μg/L	ND	ND		ND		
Cyanide	mg/L	<0.02	<0.02		<0.02		
Total organics	μg/L	ND	ND		ND		
Lead	μg/L	10,147	2,589[a]		191.4[a]		93
Nickel	μg/L	178	50.4		<19		62
Zinc	μg/L	158,110	57,950		1,430[a]		98
Total metals	μg/L	159,500	61,059		1,666		97.3
Toxicity, Minnow, 96 hr	LC_{50}	100% survival in 64%	100% survival in 64%		100% survival in 64%		
Daphnia, 48 hr	EC_{50}	>16	>16		>32		

TABLE 14. CONTINUOUS CASTING POLLUTANT REDUCTION, PLANT B

Component	Units	PSP;	SS; Δ	FDW; Δ	CT:	RC	Percent reduction
Flow	m^3/min		13.25	13.25			
pH	S.U.		6.0	5.0			
Ammonia	mg/L		<0.4	<0.4			
Oil and grease	mg/L		25.7	27.7			
Phenol 4(AAP)	mg/L		0.05	<0.02			760
Residual chlorine	mg/L		<0.2	<0.2			
Total suspended solids	mg/L		29	30			
Benzene	µg/L		ND	ND			
Naphthalene	µg/L		ND	ND			
Benzo(a)pyrene	µg/L		ND	ND			
Tetrachloroethylene	µg/L		ND	ND			
Cyanide	mg/L		<0.02	<0.02			
Total organics	µg/L		ND	ND			
Lead	µg/L		8.0	6.5			18.8
Nickel	µg/L		<4.6	<4.6			
Zinc	µg/L		96	66[a]			31.3
Total metals	µg/L		157.8	117.2			26
Toxicity, Minnow, 96 hr	EC_{50}		100% survival in 100% waste	100% survival in 100% waste			
Daphnia, 48 hr	EC_{50}		100% waste killed 65%	100% waste killed 60%			

TABLE 15. CONTINUOUS CASTING: POLLUTANT REDUCTION, PLANT E

Component	Units	PSP;	† SS; Δ	FDS ;	RC	Percent reduction
Flow	m^3/min		2.27	2.27		
pH	S.U.		7.8	7.7		
Ammonia	mg/L		2.3	<0.4		83
Oil and grease	mg/L		<1.0	<1.0		--
Phenol 4(AAP)	mg/L		0.03	0.03		--
Residual chlorine	mg/L		<0.2	<0.2		
Total suspended solids	mg/L		77	10		87
Benzene	µg/L		ND	ND		
Naphthalene	µg/L		ND	ND		
Benzo(a)pyrene	µg/L		ND	ND		
Tetrachloroethylene	µg/L		ND	ND		
Cyanide	mg/L		<0.02	<0.02		0
Total organics	µg/L		ND	ND		
Lead	µg/L		5.4	5.4		0
Nickel	µg/L		1,280[a]	1,190[a]		7
Zinc	µg/L		360[a]	300[a]		17
Total metals	µg/L		4,950[a]	4,885[a]		1.2
Toxicity, Minnow, 96 hr	LC_{50}		2.4	2.75		
Daphnia, 48 hr	LC_{50}		6.2	6.6		

TABLE 16. HOT FORMING, HOT STRIP, COLD ROLLING: POLLUTANT REDUCTION, PLANT A

Component	Units	Scale pit 3 ;	Cold roll sump ;	Cold roll scalp →	FLP;FLA;	Other wastewater ↓ CL;CNT;SS	SB;RC	Percent reduction
Flow	m^3/min	75.7	0.15	2.3	78	78	416	
pH	S.U.	7.7	7.7	5.6		7.5	7.7	
Ammonia	mg/L	<0.4	-	-		1.2	<0.4	
Oil and grease	mg/L	<0.4	8,109	5,158	153 (88)^a	18	17.8	88.4
Phenol (4AAP)	mg/L	<0.06	-	-		<0.06	<0.06	
Residual chlorine	mg/L	<0.2	-			<0.2	0.2	
Total suspended solids	mg/L	54	203	209	58.9	16 (73)	9	84.7
Benzene	μg/L	ND	ND	ND		ND	ND	
Naphthalene	μg/L	ND	ND	ND		ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND		ND	ND	
Tetrachloroethylene	μg/L	ND	ND	62.7^c		ND	ND	
Cyanide	mg/L	<0.02	-	-		<0.02	<0.02	
Total organics	μg/L	ND	ND	79.7		ND	ND	
Lead	μg/L	17.9	41^c	596^c	35	12.2 (65)	13	63
Nickel	μg/L	<19	82^c	272^c	25.6	24 (6)	<19	26
Zinc	μg/L	<28	52^c	170^c	32.3	<28 (13)	<28	13
Total metals	μg/L	105	602	2,376	173	96.5 (44)	123	29
Toxicity, Minnow, 96 hr	LC$_{50}$	100 % survived in 64%	45	17.7	-	100% survived in 64%	100% survived in 64%	
Daphnia, 48 hr	EC$_{50}$	>32	8.3	<1.0	-	>32	>32	

[a] Values in ( ) are cumulative percent reduction.

TABLE 17. HOT FORMING: POLLUTANT REDUCTION, PLANT D

Component	Units	Slabber PSP; Δ	Finish stand PSP; Δ	Rough stand PSP; Δ	SS; FDML; Δ	Percent reduction^a
Flow	m^3/min	24.6	67	10.6	102.2	
pH	S.U.	8.6	7.95	-	8.05	
Ammonia	mg/L	2.5^d	3.4^d	2.0^d	1.8^d	41
Oil and grease	mg/L	12.6	7.8	8.4	7.0	22.3
Phenol (4AAP)	mg/L	0.07	0.08	0.04	0.07	4.7
Residual chlorine	mg/L	<0.2	<0.2	NA	<0.2	
Total suspended solids	mg/L	117	203	28	23	86
Benzene	μg/L	ND	ND	ND	ND	
Naphthalene	μg/L	ND	ND	ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	
Total organics	μg/L	ND	ND	2.2	ND	
Lead	μg/L	8.6	25.5	6.6	10.6	45.6
Nickel	μg/L	75^d	179^d	83^d	71^d	50.7
Zinc	μg/L	<30	<30	30	60^d	-
Total metals	μg/L	173	265	152	171	
Toxicity, Minnow, 96 hr	LC$_{50}$	100% survived in 100%	100% survived in 100%	-	35.4^b	
Daphnia, 48 hr	EC$_{50}$	100% killed in 60%	100% survived in 100%		5.7^c	

[a] Based on composite of slabber, finish train, and rough stand, all combined for treatment.

TABLE 18. HOT FORMING: POLLUTANT REDUCTION, PLANT F

Component	Units	Universal mill PSP; Δ	Hot strip finish stand PSP; Δ	SB; SS; Δ	FDSP Δ	Percent reduction
Flow	m^3/min	13.2	28.4	41.6	41.6[a]	
pH	S.U.	7.35	7.34	7.35	7.26	
Ammonia	mg/L	<0.04	0.6[b]	-	<0.4	-
Oil and grease	mg/L	19.9	14.0	15.9	8.0	49.7
Phenol (4AAP)	mg/L	<0.06	<0.06	<0.06	<0.06	-
Residual chlorine	mg/L	<0.5	<0.5	<0.5	<0.5	-
Total suspended solids	mg/L	28	41	37	7	81.1
Benzene	µg/L	ND	ND	ND	ND	-
Naphthalene	µg/L	ND	ND	ND	ND	-
Benzo(a)pyrene	µg/L	ND	ND	ND	ND	-
Tetrachloroethylene	µg/L	ND	ND	ND	ND	-
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	
Total organics	µg/L	ND	2.3	ND	ND	-
Lead	µg/L	13.7	50.9[b]	39.1	10.4	73.4
Nickel	µg/L	691[b]	635[b]	653[b]	71.2[b]	89.1
Zinc	µg/L	28	77[b]	61.4	44	28.3
Total metals	µg/L	1,419	1,621	1,556	185	88
Toxicity, Minnow, 96 hr	LC_{50}	Nontoxic	Nontoxic			
Daphnia, 48 hr	LC_{50}	Nontoxic	Nontoxic			

TABLE 19. HOT FORMING, (SLAB MILL), HOT STRIP MILL AND CENTRAL TREATMENT: POLLUTANT REDUCTION, PLANT A

Component	Units	Slab mill PSP →	Pretreated hot strip mill, cold roll mill →	Hot strip mill PSP2[b]; Δ	Hot strip mill PSP4; Δ	Hot strip mill Δ[a]	Central treatment ST-CL; CT; SB; RC Δ	Percent reduction
Flow	m^3/min	37.9	78	102.2	65.9	284	416	
pH	S.U.	7.9		7.8	7.6		7.7	
Ammonia	mg/L	1.2[c]		<0.4	<0.4	.396	<0.4	Nil
Oil and grease	mg/L	51.5	153	23.7	11.5	60.1	17.8	70
Phenol 4(AAP)	mg/L	<0.06		<0.06	<0.06		<0.06	
Residual chlorine	mg/L	<0.2		--	--		0.2	
Total suspended solids	mg/L	94	58.9	76	15	59.6	9	85
Benzene	µg/L	ND		ND	ND		ND	
Naphthalene	µg/L	ND		ND	ND		ND	
Benzo(a)pyrene	µg/L	ND		ND	ND		ND	
Tetrachloroethylene	µg/L	ND		ND	ND		ND	
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02		<0.02	
Total organics	µg/L	ND		ND	ND		ND	
Lead	µg/L	67[c]	35[c]	8.9	67[c]	37.3[c]	13	65
Nickel	µg/L	178[c]	25.6	24	178[c]	80.7[c]	<19	76
Zinc	µg/L	57[c]	32.3	<28	57[c]	39.8	<28	30
Total metals	µg/L	601	173	118	600	309	123	60
Toxicity, Minnow, 96 hr	LC_{50}	100% survival in 64%					100% survival in 64%	
Daphnia, 48 hr	EC_{50}	Could not calculate					>32	

[a] Total from these sources to control treatment.

TABLE 20. HOT FORMING: SLAB MILL PRIMARY POLLUTANT REDUCTION, PLANT B

Component	Units	PSP Δ	E	FLP	SS Δ	Percent reduction
Flow	m³/min	18.9			18.9	
pH	S.U.	6.0			6.0	
Ammonia	mg/L	<0.4			<0.4	-
Oil and grease	mg/L	134			73.4	48.2
Phenol 4(AAP)	mg/L	<0.02			<0.02	-
Residual chlorine	mg/L	<0.2			<0.2	-
Total suspended solids	mg/L	250			22	91.2
Benzene	µg/L	ND			ND	
Naphthalene	µg/L	ND			ND	
Benzo(a)pyrene	µg/L	ND			ND	
Tetrachloroethylene	µg/L	ND			ND	
Cyanide	mg/L	<0.02			<0.02	
Total organics	µg/L	ND			ND	
Lead	µg/L	116[a]			37.9[a]	
Nickel	µg/L	157[a]			101[a]	
Zinc	µg/L	131[a]			<10	
Total metals	µg/L	792			198.6	75
Toxicity, Minnow, 96 hr	EC_{50}	100% survival in 100% effluent			100% survival in 100% effluent	
Daphnia, 48 hr	EC_{50}	100% survival in 100% effluent			100% survival in 100% effluent	

TABLE 21. HOT-FORMING BAR MILL: POLLUTANT REDUCTION, PLANT A

Component	Units	PSP; Δ	FLP;	FLA;	FLL;	A;	CL; Δ	† CT;	RC	Percent reduction
Flow	m³/min	3.8					3.8			
pH	S.U.	8.1					8.0			
Ammonia	mg/L	<0.4					<0.4			
Oil and grease	mg/L	57					17.2			70
Phenol 4(AAP)	mg/L	<0.02					0.03			
Residual chlorine	mg/L	0.2					<0.2			
Total suspended solids	mg/L	110					24			78
Benzene	µg/L	ND					ND			
Naphthalene	µg/L	ND					ND			
Benzo(a)pyrene	µg/L	ND					ND			
Tetrachloroethylene	µg/L	ND					ND			
Cyanide	mg/L	<0.02					<0.02			
Total organics	µg/L	ND					ND			
Lead	µg/L	112[a]					20			82
Nickel	µg/L	74[a]					15			80
Zinc	µg/L	<28					<28			
Total metals	µg/L	284					97			66
Toxicity, Minnow, 96 hr	LC_{50}	100% survival in 100%					100% survival in 100%			
Daphnia, 48 hr	LC_{50}	Could not calculate					Could not calculate			

TABLE 22. HOT-FORMING, SECTION MILL; POLLUTANT REDUCTION, PLANT E

Component	Units	PSP; Δ	SS ; Δ	Central treatment		Percent reduction
				RC→CPT;CYPT; NC;NA; FLP; Δ	CL;$\bar{S}\bar{S}$ Δ	
Flow	m^3/min	7.6	7.6	2.6	2.6	
pH	S.U.	7.9	7.8	10.9	7.51	
Ammonia	mg/L	1.8[b]	<0.4 (78)[a]	4.6[b]	5.8[b]	-
Oil and grease	mg/L	16.6	3.2 (88)	34.1	<1	97
Phenol (4AAP)	mg/L	0.03	<0.02 (33)	0.11	0.07	36
Residual chlorine	mg/L	<0.2[b]	<0.2[b]	<0.2[b]	<0.2[b]	
Total suspended solids	mg/L	101	61 (40)	1,046	11	98
Benzene	μg/L	ND	ND	ND	ND	
Naphthalene	μg/L	ND	ND	76.3	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	0.04	0.04	
Total organics	μg/L	ND	ND	83.7	11.9	
Lead	μg/L	31[b]	24.1 (22)	66.6[b]	<1.9	>97
Nickel	μg/L	9,350[b]	5,840 (38)[b]	62,500[b]	326[b]	99.5
Zinc	μg/L	350[b]	270 (21)[b]	90[b]	<20	78
Total metals	μg/L	10,333	6,488 (37)	232,746	492	99.8
Toxicity, Minnow, 96 hr	LC_{50}	Nontoxic	Nontoxic	2.4	65% survival in 100% sample	
Daphnia, 48 hr	LC_{50}	80% survived in 100%	60% survived in 100%	0.1%	38%	

[a] Values in parentheses are cumulative reductions.

TABLE 23. PICKLING: POLLUTANT REDUCTION, PLANT F

Component	Units	E; Δ	NL; CL Δ	Percent reduction
Flow	m^3/min	2.3	2.3	
pH	S.U.	2.45	7.45	
Ammonia	mg/L	1.9[a]	1.9[a]	
Oil and grease	mg/L	1.5	2.4	
Phenol 4(AAP)	mg/L	<0.06	<0.06	
Residual chlorine	mg/L	<0.5	<0.5	
Total suspended solids	mg/L	169	6	96.4
Benzene	μg/L	ND	ND	
Naphthalene	μg/L	ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	
Cyanide	mg/L	0.02	<0.02	
Total organics	μg/L	2.8	ND	
Lead	μg/L	8.2	2.4	71
Nickel	μg/L	14,900[a]	65.2[a]	99.6
Zinc	μg/L	72[a]	17	76.4
Total metals	μg/L	56,881	190	99.7
Toxicity, Minnow, 96 hr	LC_{50}	6.9	Nontoxic	
Daphnia, 48 hr	LC_{50}	4.3	75% survived in 100% sample	

TABLE 24. PICKLING AND COLD ROLLING: POLLUTANT REDUCTION, PLANT B

Component	Units	Pickling rinse and scrubber Δ	Cold rolling discharge Δ	SS; FLF; A; AO; NL; FLP; CL Δ	Δ	Percent reduction
Flow	m^3/min	3.8	1.9	5.3	5.3	
pH	S.U.	1	6.5	-	5.0	
Ammonia	mg/L	2.5[a]	-	-	-	
Oil and grease	mg/L	27.7	885	-	4.3	98.6
Phenol 4(AAP)	mg/L	0.04	-	-	-	-
Residual chlorine	mg/L	<0.2[a]	-	-	-	-
Total suspended solids	mg/L	7	55	-	9	60
Benzene	µg/L	ND	ND	ND	ND	
Naphthalene	µg/L	ND	ND	ND	ND	
Benzo(a)pyrene	µg/L	-	ND	ND	ND	
Tetrachloroethylene	µg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	-	-	-	
Total organics	µg/L	ND	2.2	3.2	3.9	
Lead	µg/L	15.1	7.6	17.2	<1.9	85
Nickel	µg/L	375[a]	98.2[a]	199[a]	12.3	96
Zinc	µg/L	126[a]	46	91[a]	<10	90
Total metals	µg/L	1,900	365	835	84	90
Toxicity, Minnow, 96 hr	LC$_{50}$	8.84	80% survival in 100% waste		100% survived in 100% waste	
Daphnia, 48 hr	EC$_{50}$	90% killed in 6.25%	100% killed in 95% waste		100% killed in 95% waste	

TABLE 25. COLD FORMING, ONCE THROUGH TANDEM MILL: POLLUTANT REDUCTION, PLANT A

Component	Units	SB; Δ	SS; Δ	CNT	Percent reduction
Flow	m^3/min	0.6	0.6		
pH	S.U.	8.0	7.7		
Ammonia	mg/L	-	-		
Oil and grease	mg/L	566	217		62
Phenol 4(AAP)	mg/L				
Residual chlorine	mg/L				
Total suspended solids	mg/L				
Benzene	µg/L	ND	ND		
Naphthalene	µg/L	30	32.4		-
Benzo(a)pyrene	µg/L	ND	ND		
Tetrachloroethylene	µg/L	3.6	5.1		-
Cyanide	mg/L	-	-		-
Total organics	µg/L	80.1	88.9		-
Lead	µg/L	42[b]	10		76
Nickel	µg/L	37.3	11		71
Zinc	µg/L	<28	<28		-
Total metals	µg/L	206	87		58
Toxicity, Minnow, 96 hr	LC$_{50}$	100% survival in 100% waste	100% survival in 100% waste		
Daphnia, 48 hr	EC$_{50}$	could not be calculated	4.2		

TABLE 26. HOT COATING, GALVANIZING: POLLUTANT REDUCTION, PLANT C

Component	Units	E; Δ	NL;	FLP;	VF CL Δ	Percent reduction
Flow	m^3/min	4.9			4.9	
pH	S.U.	2.8[a]			7.5	
Ammonia	mg/L	21.9[a]			18.5[a]	15.5
Oil and grease	mg/L	1.4			1.4	
Phenol 4(AAP)	mg/L	<0.02			<0.02	
Residual chlorine	mg/L	<0.2			<0.2	
Total suspended solids	mg/L	115			2	98.3
Benzene	μg/L	ND			ND	
Naphthalene	μg/L	ND			ND	
Benzo(a)pyrene	μg/L	ND			ND	
Tetrachloroethylene	μg/L	ND			ND	
Cyanide	mg/L	0.07			0.03	57.1
Total organics	μg/L	ND			ND	
Lead	μg/L	149[a]			<2	98
Nickel	μg/L	65[a]			10	85
Zinc	μg/L	99,000[a]			2,330[a]	97.6
Total metals	μg/L	100,816			2,422	
Toxicity, Minnow, 96 hr	LC_{50}	3.9			100% survival in 100% waste	
Daphnia, 48 hr	EC_{50}	4.1			100% survival in 100% waste	

IRONMAKING

Toxicity does not seem to derive from pH or high concentration of priority pollutants. Very little reduction in toxicity occurs from reductions in metals (Plant A). The high residual chlorine may have caused higher toxicity for plant A. This suggests that chlorination (the final treatment) might best be omitted.

STEELMAKING

For very similar treatments, the treated wastewaters from wet open combustion were less toxic than those from suppressed combustion.

CONTINUOUS CASTING

The same treatment processes were employed at both plants. The effluent with higher metal loadings showed higher toxicity.

HOT FORMING

Treated wastewaters showed little toxicity or no toxicity, except in two cases, for minnows. All showed higher toxicity to daphnia. There is no clear correlation of toxicity with pollutant levels except for the section mill, where toxicity, ammonia, phenol, nickel and cyanides were all higher than for the other treated wastewaters, and the total organics were relatively the highest.

PICKLING

Treated wastewaters were non-toxic to minnows. Daphnia showed 75 percent survival in one case, and about 45 percent kill in the other. Very little difference in pollutant loads was observed.

COLD FORMING

The treated wastes showed no toxicity to minnows: EC_{50} of 4.2 to daphnia. Naphthalene and tretrachloroethylene were high; other pollutants, very low.

HOT COATING

Treated waters were non-toxic despite relatively high ammonia and zinc concentrations. Cyanides were low, and total organics were not detected (ND).

CENTRAL TREATMENT

These systems showed moderate toxicity for minnows (No LD_{50} in one case; LD_{50} > 64 in the other). Daphnia toxicity, EC_{50}, was 32 to 38.

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USE OF TOXICOLOGICAL TESTING IN THE WATER REGULATORY PROGRAM

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ABSTRACT

EPA and the States have become increasingly interested in the use of toxicological testing techniques to assess and control the impacts of wastewater discharges on receiving waters. These techniques have a significant advantage over chemical testing in certain situations because they measure the effects of all pollutants and their interactions in complex effluent/receiving water matrices. This paper describes the advantages and limitations of available methods, how EPA is planning to use these techniques in the regulatory program, and the considerations involved in interpreting results. Criteria for excessive toxicity and the use of Toxicity Reduction Evaluations to identify engineering solutions for toxicity problems are discussed. Current policy developments are also described.

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INTRODUCTION

As the water pollution control effort in the United States progresses and the "traditional" pollutants (oxygen demanding and eutrophying materials) become sufficiently treated to protect water quality, attention is shifting towards pollutants that impact water quality through toxic effects. Compared to the traditional pollutants, little is known about pollutants that are toxic to aquatic life. Some of the difficulties associated with controlling these pollutants involve determining whether such pollutants are being discharged and what the effects of the pollutants are in complex effluent and receiving water matrices. This paper discusses the use of general toxicological effects tests that can be applied to effluent and receiving water samples to measure toxicity and, thereby, provide a means to assess and control discharges of toxic pollutants.

WHY TOXICITY TESTING

The most common approach for assessing and controlling water pollution is based on measuring and limiting the discharge of individual chemicals. Under this approach, analyses are conducted to determine the concentrations of pollutants in water samples. Concentration standards based on the biological effects and chemistry of the individual pollutants are developed to protect water quality The ability of treatment processes to remove the pollutants from wastewaters can also be studied in a direct manner.

There are several problems associated with this chemical-specific approach that become apparent when dealing with toxic pollutants. The first problem is the great number of toxic chemicals that may potentially be discharged to receiving waters and the difficulties in their analysis. The second problem is that the toxic effects of a chemical are often dependent on the matrix of constituents in which it exists. Toxic chemicals by their nature are reactive. If substances which bind or otherwise change the chemistry of the pollutant are present in the water matrix, the availability to aquatic organisms will be altered. Finally, aquatic organisms are rarely exposed to a single toxic pollutant. An effluent will have many chemicals and characteristics (including temperature and pH) that can affect the physiology of exposed organisms. It is often impossible to predict the effect of exposure to combinations of chemicals.

Toxicity testing is a means to overcome these problems. A toxicity test provides a direct measurement of water quality effects. These tests are conducted by exposing test organisms to water samples for a specific time period under controlled conditions. There are two ways to quantify effects: (1) the degree of impairment of the organisms when exposed to a single sample can be measured and (2) organisms can be exposed to a series of dilutions and the dilution at which a particular effect endpoint occurs determined. Several organisms are exposed to each concentration and adequate replicates and controls are used. When toxicity tests are conducted using receiving water for diluant, the test accounts for any interactions that occur between effluent constituents and receiving water constituents.

Because toxicity tests measure effects without identifying causitive agents, toxicity analyses are not unlike the analysis for biochemical oxygen demand (BOD). BOD is used extensively as an indicator of receiving water effects without concern for the organic constitutents that make up the sample or their individual oxygen demanding reactions. Likewise, toxicity can be used as an indicator of receiving water effects and as a parameter for controlling discharges.

WHERE DO THESE METHODS FIT IN THE REGULATORY PROCESS

Toxicity tests have been in use for centuries. One of the earliest applications was the use of canaries to detect hazardous gaseous conditions in Roman mines. Aquatic organism tests were developed in the early part of this century. They have been used extensively to develop "safe levels" or criteria for individual chemicals to set water quality standards. Aquatic toxicity tests have not been used extensively to test effluents. When toxic pollutants have been controlled, the basis has usually been aquatic criteria and simplifying assumptions about fate, bioavailability, and combined pollutant toxicity.

Because a water quality impact assessment is a case-by-case analysis, the proper context is the discharge permit review process. Figure 1 presents a simplified flow diagram of the water quality-based permit development process.

As can be seen in the flowchart, the basis for evaluating discharges and imposing controls is State water quality standards. Every State has developed a classification system of "designated uses" for their water bodies. The classified uses define what is to be protected, and range from irrigation water supply to propagation of aquatic life. Toxicity test methods are used to measure impacts in relation to the protection of aquatic life. Many States also include specific numerical criteria in their water quality standards to protect a particular designated use. Some State standards have toxicity criteria. When criteria (either chemical or toxicity) are absent, the regulatory authority must use judgment to define requirements that will protect the use.

The decision to use toxicity tests will depend on the discharge situation. The Environmental Protection Agency (EPA) is recommending that these methods be used for complex effluents containing many pollutants and where the effects of mixing are important such as in multiple

Figure 1. Water Quality Permitting Flowchart

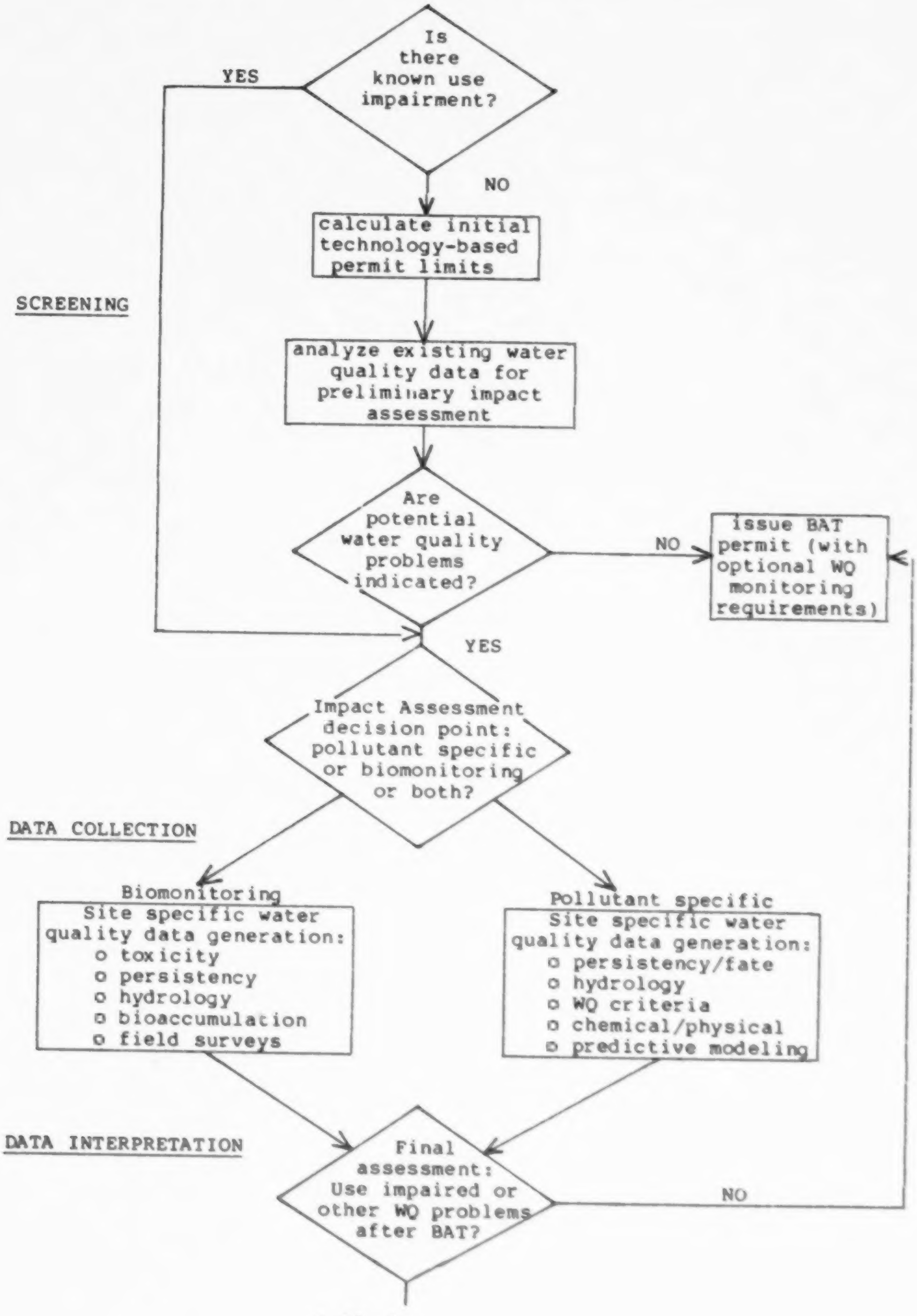
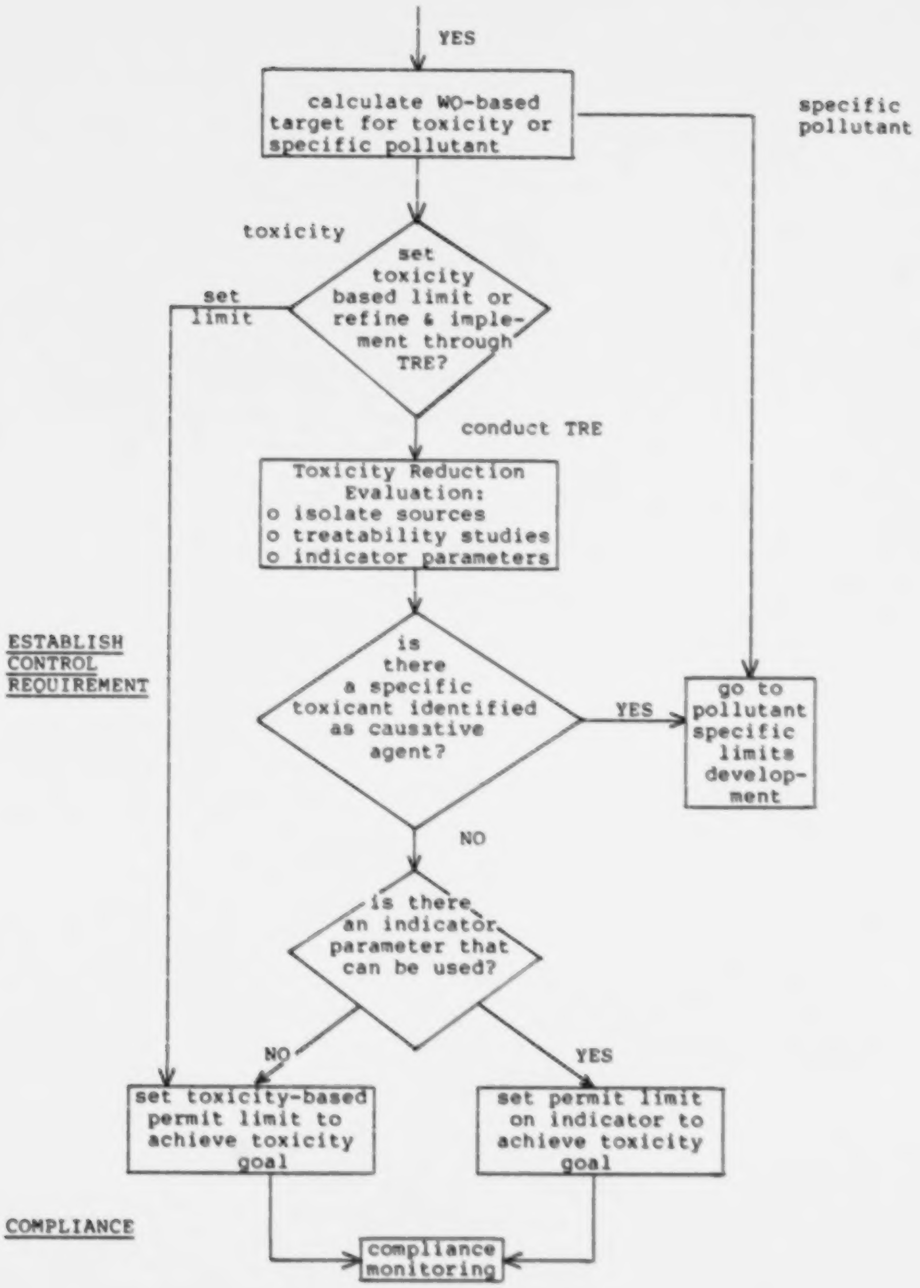

Is there known use impairment?
YES
NO
calculate initial technology-based permit limits
SCREENING
analyze existing water quality data for preliminary impact assessment
Are potential water quality problems indicated?
NO
issue BAT permit (with optional WQ monitoring requirements)
YES
Impact Assessment decision point: pollutant specific or biomonitoring or both?
DATA COLLECTION
Biomonitoring
Site specific water quality data generation:
o toxicity
o persistency
o hydrology
o bioaccumulation
o field surveys
Pollutant specific
Site specific water quality data generation:
o persistency/fate
o hydrology
o WQ criteria
o chemical/physical
o predictive modeling
DATA INTERPRETATION
Final assessment: Use impaired or other WQ problems after BAT?
NO

Figure 1. (cont.)


YES
calculate WQ-based target for toxicity or specific pollutant
specific pollutant
toxicity
set toxicity based limit or refine & implement through TRE?
set limit
conduct TRE
Toxicity Reduction Evaluation:
o isolate sources
o treatability studies
o indicator parameters
ESTABLISH CONTROL REQUIREMENT
is there a specific toxicant identified as causative agent?
YES
go to pollutant specific limits development
NO
is there an indicator parameter that can be used?
NO
YES
set toxicity-based permit limit to achieve toxicity goal
set permit limit on indicator to achieve toxicity goal
COMPLIANCE
compliance monitoring

source situations. For simple effluents, chemical-specific methods are probably more cost effective.

CONDUCTING A WATER QUALITY ASSESSMENT USING TOXICITY

When a screening level review has indicated a potential water quality problem, an assessment of water quality is necessary. An assessment consists of two principal parts -- analysis of the effluent and analysis of the exposure. Where multiple sources are involved, an additional aspect of changes in the instream toxicity due to effluent mixing may be considered.

Effluent toxicity to one or several test organisms must be determined together with an assessment of the variability of the toxicity. Effluent toxicity is usually measured as the effluent dilution (in percent effluent) that results in a particular toxicity endpoint such as no chronic effects or 50% lethality. Adjustment factors are often used to estimate one effect concentration from data on a different effect. For example, the concentration difference between 50% lethality and no effect on growth or reproduction is termed the acute-to-chronic ratio and is used to estimate safe concentrations from acute toxicity data.

Exposure is the other half of the assessment and is determined by examining stream flow in relation to effluent flow. EPA is developing statistical methods based on probability to examine the frequency that a particular effluent concentration threshold will be exceeded based on hydrology and effluent variability. Alternatively, a "standard" low flow measure, such as the 7Q10, may be used to evaluate dilution. Both of these methods assume complete mixing. When mixing is slow (e.g., discharges to large rivers where shore-hugging plumes may extend many miles), effluent dispersion at low flow may be measured and used to determine zones of acute and chronic toxicity. These zones are then compared to the allowed mixing zone, or "allocated impact zone." Exposure, measured either by the low flow dilution assuming complete mixing or the effluent dispersion vs. mixing zone approaches, determines whether the measured effluent toxicity is acceptable or unacceptable.

Methods for measuring effluent acute toxicity (lethality) have been standardized and available for many years. However, effects on growth and reproduction (chronic toxicity) are of primary concern because these important effects occur at lower concentrations than those which cause lethality. Until recently, chronic tests were much more expensive than acute tests. However, newly developed short-term chronic tests are making practical the testing of ambient receiving waters and effluents in situations where acute tests can not be used because of low receiving water dilution.

There are several important considerations involoved with designing an assessment and applying the results. These are currently being studied by EPA and are summarized below:

1. Species sensitivity - How many organisms should be tested to assure that the more sensitive organisms in the aquatic community are represented? Different organisms respond differently to toxic pollutants. The more species used to characterize the toxicity of an effluent, the greater certainty you can have that the range of sensitivity has been approximated. Some minimum data set will be established but at least two species (a vertebrate and an invertebrate) should be used.

2. Acute-to-chronic ratio - Acute tests are often used because of lower testing costs. The acute-to-chronic ratio is used to estimate chronic toxicity from acute data. Very little data on acute-to-chronic ratios for effluents has been developed. From the chemical data, it appears that a reasonable estimate of the ratio would be between 10 and 100.

3. Effluent variability - Variability must be measured or estimated to assess water quality impacts. Potential variability should be considered when deciding the frequency and duration of testing. If limited data is available, a safety factor might be used to estimate worst case toxicity.

4. Multiple sources - How do you account for the mixing of several effluents in a receiving water? One approach is to assume that toxicity is additive using the following formula:

   $$\text{toxicity of mixture} = \sum(\text{individual effluent toxicity} \times \text{its proportion in the mixture})$$

   Available data suggest additivity is a reasonable assumption but the assumption can be tested by measuring the toxicity of the individual effluents and then measuring the toxicity of ambient samples or a mixture of effluents and receiving water. Chronic toxicity tests must often be used because of insufficient sensivity of acute tests.

5. Persistency - Most toxic pollutants are removed or degraded over time. Therefore, water quality impacts can be expected to be reduced at some rate. For an assessment of toxicity, the duration of the toxic effect is of concern in determining the size of the impact zone and the extent to which multiple sources may contribute to cumulative impacts. However, where biological treatment is employed, effluents are usually stable and any toxicity effects will not decrease rapidly. Therefore, if we separate the receiving water into "near field" and "far field", we can make the assumption that toxicity is conservative (does not degrade) within the "near field".

WHAT IF PROBLEMS ARE INDICATED

Where water quality standards are not being attained, the regulatory authority will calculate effluent requirements to attain the standards. These requirements represent a goal which will provide attainment of the water quality standard. They may or may not become permit limits. In most cases, the required effluent toxicity is based entirely on the available (or allowed) dilution in the receiving water. The effects of other sources may be considered if the sources are contributing to the degradation.

When it comes to implementing a toxicity goal through permit conditions, there are several options. One is to incorporate the toxicity requirement into the permit as an enforceable toxicity limit. Another option is to require a toxicity reduction evaluation to identify effective control techniques and try to identify causative pollutants or indicator parameters for permit limits. The advantage of identifying a chemical parameter for limitation as opposed to toxicity is that more compliance monitoring can often be conducted at lower cost.

A toxicity reduction evaluation (TRE) is an engineering study in which toxicity is used as the analytical parameter. Such studies should be conducted by permittees because of their greater familiarity with their facilities. A TRE consists of two aspects: attempting to identify the sources or causes of the toxicity in the final effluent; and determining the effectiveness of various control alternatives for reducing toxicity. Identifying causitive pollutants is not necessary but may lead to cost effective controls such as process modification. The key part of a TRE is determining the effectiveness of control alternatives to reduce toxicity to the level necessary to meet standards. Once a sufficient control option is identified, an indicator parameter to implement the option should be considered. An example might be TOC limits to ensure operation of carbon adsorption.

CURRENT STATUS

The use of toxicity testing to evaluate water quality impacts is not yet widespread but is increasing. We estimate that about five hundred permits include toxicity testing as a monitoring requirement. Considerably fewer permits include toxcity limits. Part of the reason EPA Regions and the States have not used toxicity permit limits is confusion about EPA's policy on such limits. To correct this problem, EPA is planning to issue a policy on toxic pollutants which endorses the use of effluent toxicity as a control parameter. A draft of this policy was circulated for comment on September 9, 1983.

Many States are now in the process of developing their own State policies on toxic pollutants and the use of toxicity testing. The Association of State and Interstate Water Pollution Control Administrators is also working on a policy statement calling for increased use of effluent toxicity as a pollution control parameter.

EPA is also preparing a technical support document on water quality-based controls for toxic pollutants. A workshop of experts from industry, academia, and government has been held to discuss a preliminary draft of the document. Another draft will be available for review by the end of the year. The application of toxicity testing is being supported by an active research program consisiting of methods development and standardization, basic research on toxicology, and field studies to test procedures and assumptions and verify the relationship between effluent toxicity and instream impacts.

IRON AND STEEL CASE STUDY

Iron and steel wastewaters generally are fairly simple. The notable exception is coke making wastewaters. Discharges containing coke wastewater are the most likely candidates for evaluation using toxicity. Another feature of iron and steel discharges is clustering of several plants in close proximity. Multiple sources complicate an assessment of water quality because the combined effects must be considered. In these situations, toxicity data may have to be generated for all sources and toxicity tests of instream samples may be necessary.

The following case study illustrates the use of toxicity testing to evaluate water quality effects. The site is the Five Mile Creek near Birmingham, Alabama. The stream is classified for industrial use and, therefore, no requirements based on water quality would be imposed unless the standards were upgraded. The site was selected for its suitability for research purposes.

Figure 2 illustrates the study site. Three discharges were evaluated -- a municipal sewage treatment plant, and two coke making plants. The following data were collected during a one week period: hydrology; effluent acute and chronic toxicity to fathead minnows and Ceriodaphnia; chronic toxicity of ambient samples taken from 12 points in the river; and health of the aquatic community as measured by ecological survey. Flow rate and dilution information for the discharges are presented in Table 1. Several storm events occurred during the study and interefered with the hydrology and confirmatory instream work. Therefore, the dilution data in Table 1 are estimated based on the 7 day average low flow expected in 10 years (7Q10).

The first step is to determine whether water quality is impacted. All available data (chemical monitoring, ecological surveys, citizen complaints) should be used to make this assessment. Some preliminary effluent toxicity data are presented in Table 2. In evaluating toxicity data, the effluent concentration which causes no observable effect is compared to the effluent concentrations existing in the receiving water.

Detailed ecological surveys were conducted for fish, benthos, and periphyton to provide the validation data for the field study. Data on the fish community are shown in Figure 3. The data show impact and recovery below each discharge. The STP discharge appears to have significantly less effect on the fish community compared to the two coking plants.

Comparable data for the benthic community are presented in Figure 4. These data indicate an impact between Stations 1 and 2 prior to the ABC discharge. Below ABC the response becomes complicated. Diversity is reduced below ABC but community loss is improved. Similarly, the number of species and abundance of organisms increases. Both J. Walters discharge and the STP cause decreases in the number of species and abundance but increase divesity.

The third part of this study was toxicity analyses of samples collected instream to gain insight into the persistency of toxicity and interactions between effluents. These instream tests were not dilution series tests and, therefore, provide only a relative measure of toxicity. The growth data for the fathead minnow tests and the reproduction data for the *Ceriodaphnia* tests are presented in Figures 5 and 6. As mentioned above, storm events caused high flow conditions which reduced the instream toxicity (e.g., flow during the study at Station 7 ranged from 117 to 395 cfs).

The fish and invertebrates responded differently to the instream samples. Upstream water and waters below ABC and the STP impaired the growth of minnows. For *Ceriodaphnia* reproduction, upstream water and waters below J. Walters and the STP were highly toxic while the ABC discharge mitigated the upstream toxicity. This mitigation of river water toxicity can also be seen in the effluent toxicity tests. One likely explanation is that metals are present in the upstream water which are complexed by the coking waste.

From this data it would be concluded that all three plants discharge effluents with excessive toxicity for the dilution available at low flow. The next step is to calculate acceptable effluent toxicity levels to acheive no-effect after dilution at the flow specified by the water quality standards. If each discharge were considered independently (ignoring cumulative effects), the following relationship would be used:

$$\text{effluent no-effect concentration (in \%)} > \frac{\text{Effluent flow} \times 100}{\text{Total flow}} \times \text{SF}$$

In this case the regulatory authority might decide that no safety factors (SF) are necessary for the following reasons: the toxicity measurement must be specified as chronic toxicity because of low dilution; the plants have large treatment systems and low variability; and two species have been tested and the more sensitive would be used. The requirement can be expressed either as the minimum allowable percent effluent causing no-effect or as the maximum allowable Toxic Units. A Toxic Unit is simply the inverse of the effluent dilution causing no-effect.

For this example, the toxicity requirements would be based on the *Ceriodaphnia* test. If requirements were calculated by assuming no cumulative effects of the multiple sources, the requirements would be as follows:

Alabama By-Products - no-effect at 6.0% effluent; or 16 T.U.
J. Walters Coking - no-effect at 50% effluent; or 2 T.U.
Five Mile Creek STP - no-effect at 60% effluent; or 1.7 T.U.

However, because this is a multiple source situation, the cumulative effects of the effluents should be considered. A conservative evaluation of the requirements calculated above can be conducted by assuming that toxicity is persistent and additive. Using these assumptions, the instream toxicity at Station 7 can be calculated as follows:

$$\begin{aligned} \text{Stream toxicity (T.U.)} &= \sum (\text{T.U.} \times \text{proportion in final mixture}) \\ \text{Station 7 instream tox.} &= (16 \times 0.006) + (2 \times 0.12) + (1.7 \times 0.6) \\ &= 1.35 \text{ Toxic Units} \end{aligned}$$

To have no toxic effects, the instream toxicity would have to be 1.0 Toxic Unit or less. The cumulative effects in this case might be investigated further. Additional instream toxicity tests during low flow conditions are one way to assess whether cumulative effects are important.

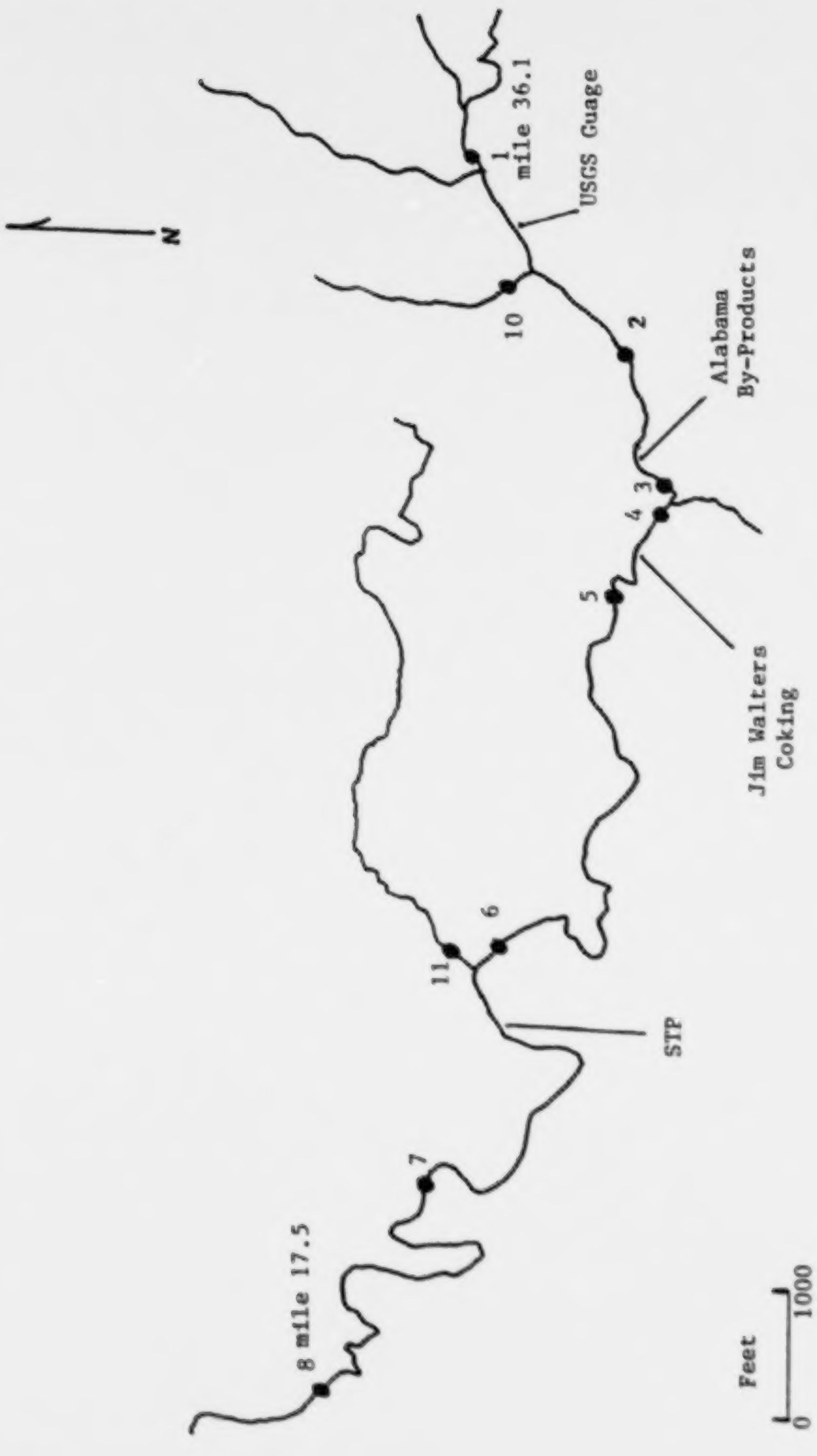

N
1
mile 36.1
USGS Guage
10
2
Alabama
By-Products
3
4
5
Jim Walters
Coking
6
11
STP
7
8 mile 17.5
Feet
0
1000

Figure 2. Discharges and sampling stations, Five Mile Creek

Table 1. Flow and dilution at the 7Q10 low flow, Five Mile Creek

Location	Flow [1]	Percent Contribution ABC	Percent Contribution J. Walters	Percent Contribution STP
USGS Gauge	4.0			
ABC discharge	0.3			
Station 3	5.0	6.0		
J. Walters discharge	6.0			
Station 5	12.0	2.5	50	
Station 6	15.0	2.0	40	
Above STP	18.0			
STP discharge	30.0			
Station 7	50.0	0.6	12	60

[1] All flows are cfs; stream flows estimated for 7Q10 low flow

Table 2. Preliminary toxicity data for three effluents, Five Mile Creek

Toxicant + Dilution[2] Water	No Effect Concentrations (% effluent)[1] Fathead Minnows survival	Fathead Minnows growth	Daphnia survival	Daphnia #young
ABC + river water (2a)	1.0	0.5	1	*
ABC + well water	0.5	0.5	1	<.5
J. Walters + river water (3)	50	5	50	5.0
J. Walters + well water	50	10	50	1.0
J. Walters + river water (1)	50	10	-	-
STP + river water (6)	100	100	5	10

[1] highest concentration where no effect was observed
[2] parentheses indicate station where river water was obtained
* river water caused reduced young production

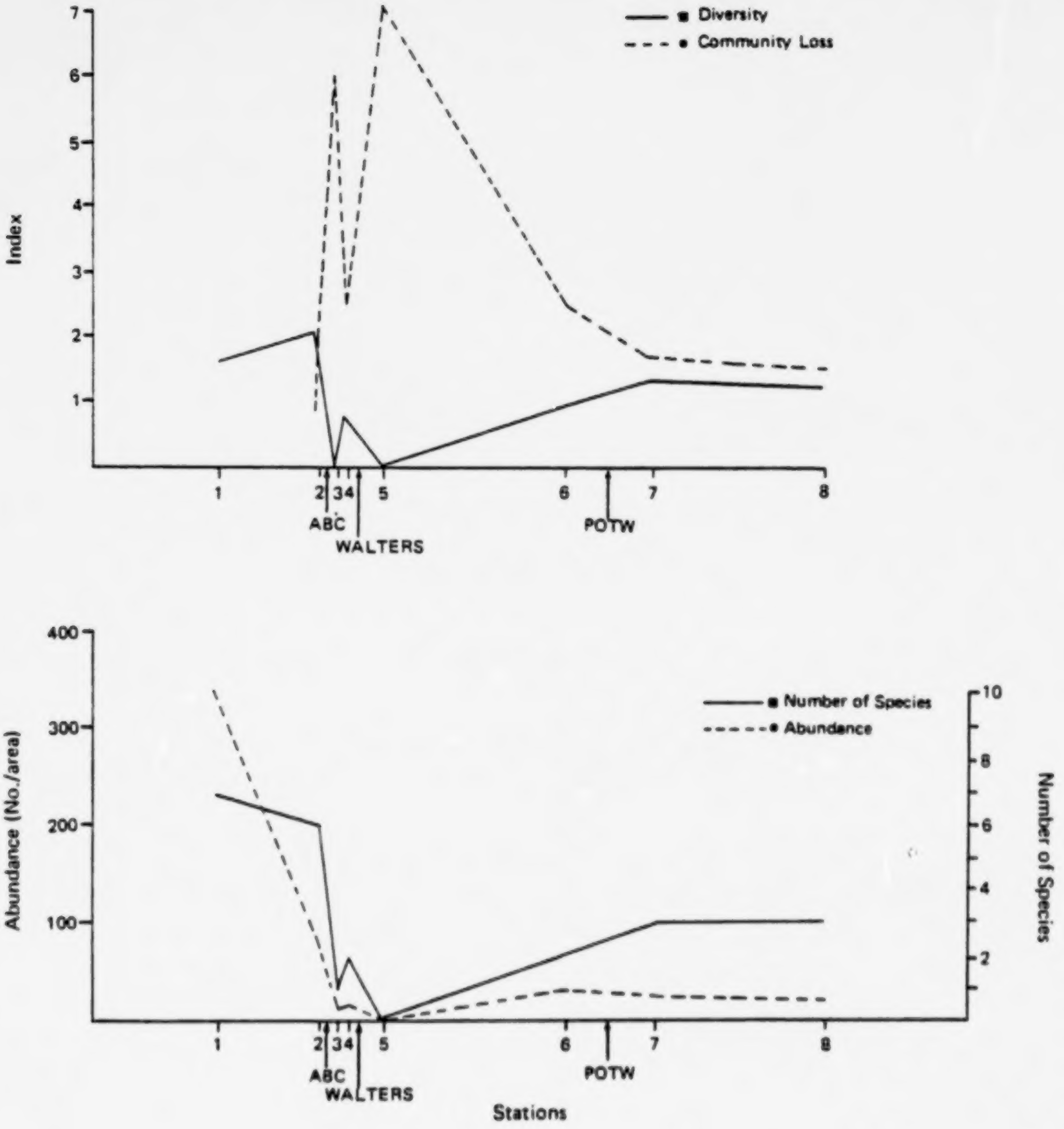


Figure 3. Fish species diversity, community loss, and components of these indices, Five Mile Creek

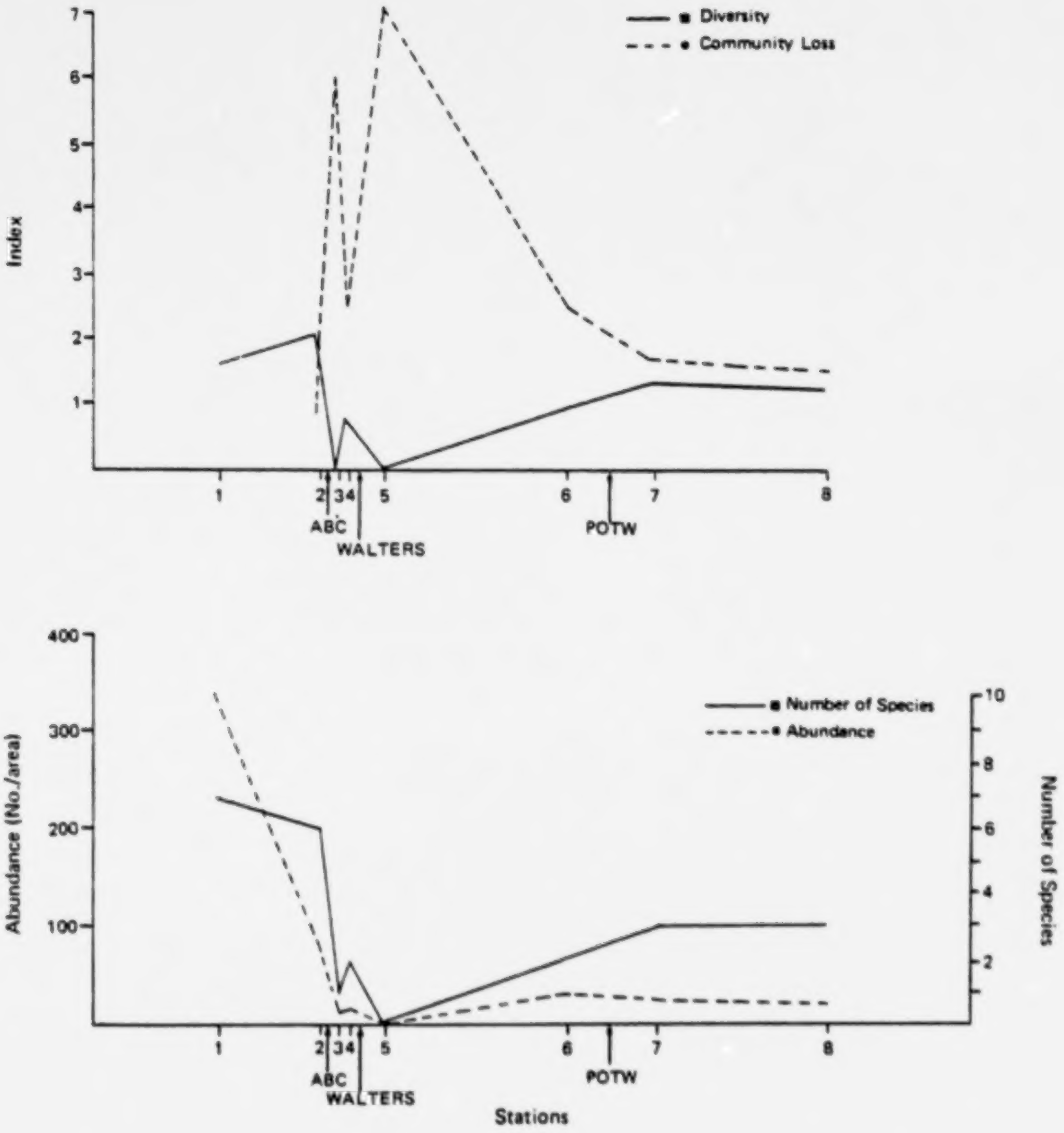


Figure 3. Fish species diversity, community loss, and components of these indices, Five Mile Creek

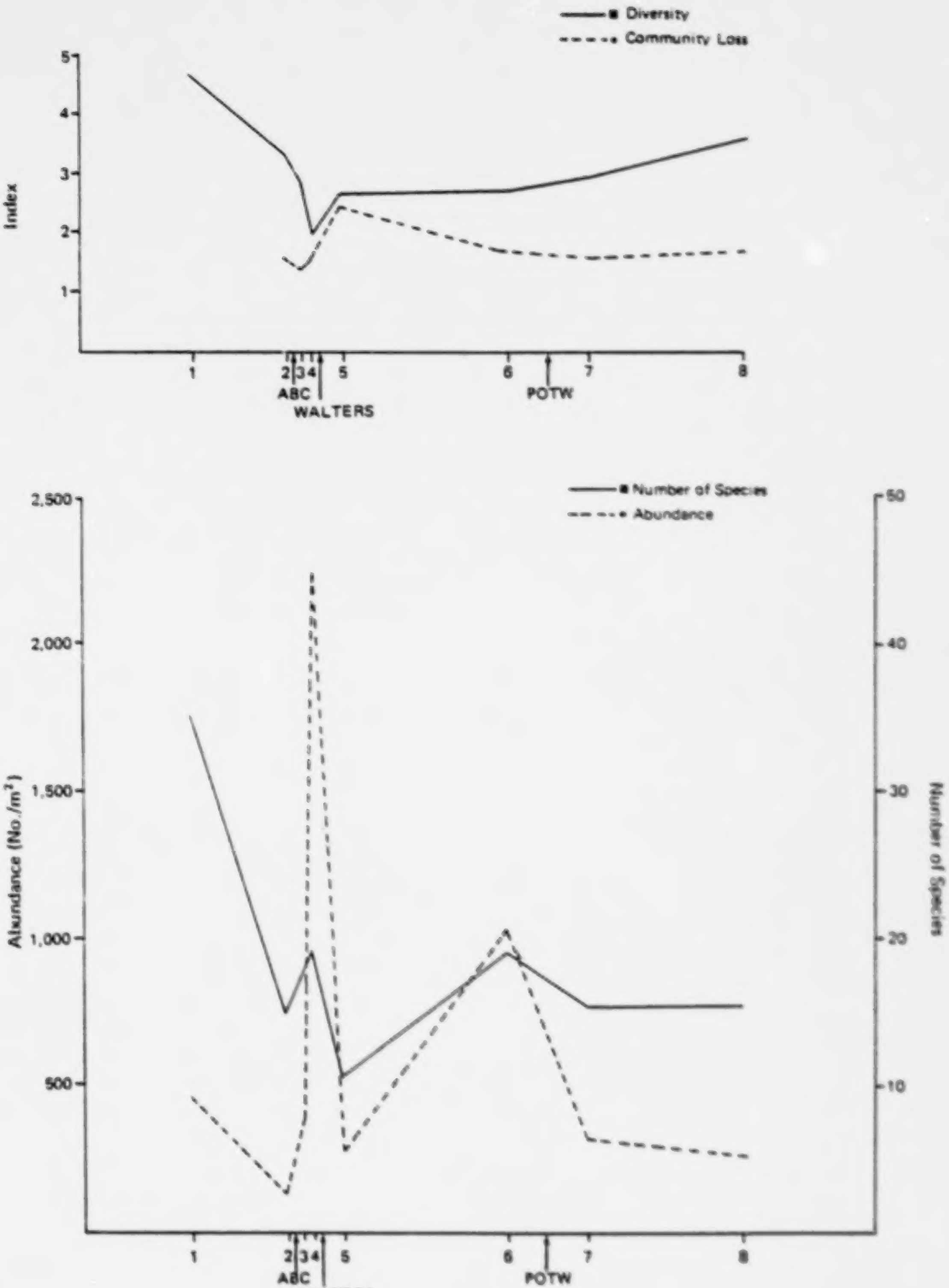


Figure 4. Benthic species diversity, community loss, and components of these indices, Five Mile Creek

FIGURE 5. Fathead Minnow Weights for Instream Stations

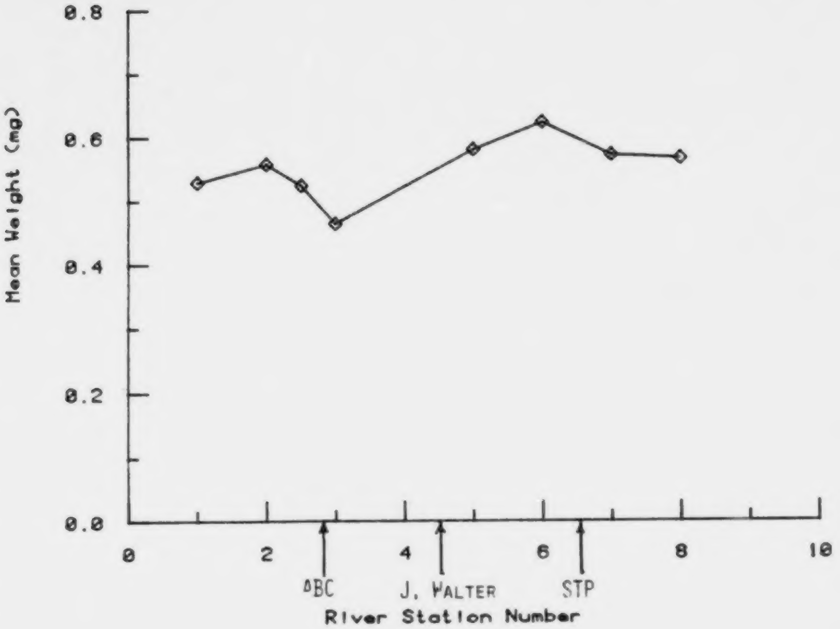
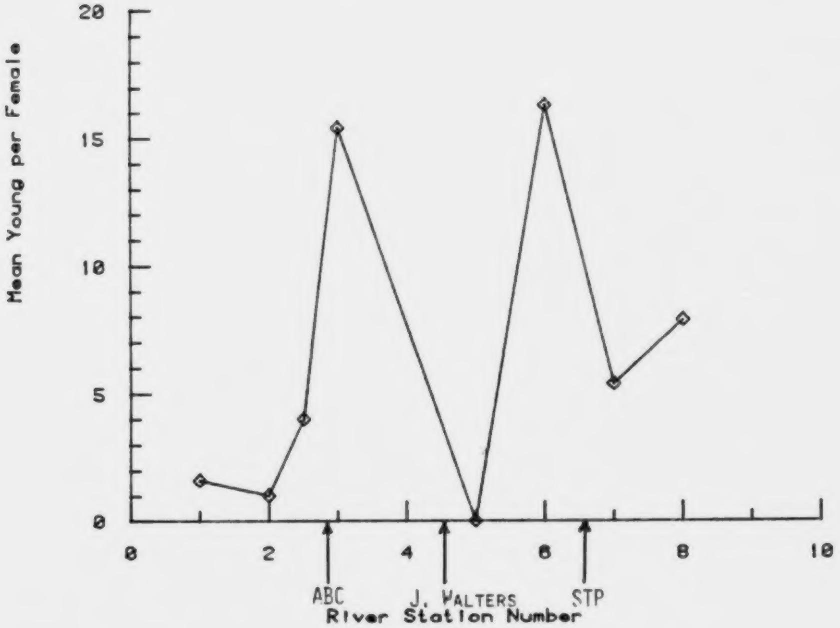


FIGURE 6. Young Production for Alabama Instream Stations



SESSION 2

AIR POLLUTION ABATEMENT

CHAIRMEN:

Richard Dworek
U.S. Steel Corporation
Monroeville, PA 15146

and

William M. Smith
National Steel Corporation
Pittsburgh, PA 15219

COMPARATIVE EVALUATION OF INSTALLED PUSHING EMISSIONS CONTROL TECHNOLOGIES

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ABSTRACT

Results of a detailed analysis of operating and maintenance problems encountered by coke producers during startup and operation of mobile scrubber cars and sheds are presented. Availability and emissions data compiled to date for all pushing control systems are provided. An update on the current status of pushing emissions controls and a description of recent events are provided, with emphasis on sheds and mobile scrubber cars.

Although the information in this document has been funded, wholly or in part, by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review. Therefore, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

INTRODUCTION

Over the past 10 years, the U.S. coke industry has expended over 500 million dollars to install equipment to control pushing emissions from coke oven batteries (1). Substantial expenditures have also been incurred to debug, operate and maintain the control equipment. Throughout the 1970s, push control technology steadily evolved from engineering concepts and demonstration units into the current state-of-the-art techniques. To date, push control systems have been installed on approximately 80 percent of all batteries operable or potentially operable in mid-1983. These installations represent three generic types of technology, i.e., mobile scrubber cars, sheds, and fixed duct systems with land-based gas cleaners. Within the three generic categories are approximately 16 different systems, plus several modifications to each push control system type.

Pushing control technology has been described in the technical literature, and also evaluated in detail by coke producers prior to selecting equipment. However, an in-depth, comparative analysis of operating experience with each system type has not been performed to date. Consequently, GCA/Technology Division is currently comparing all push control technologies by evaluating the following: system design variables; start-up, operation and maintenance (O&M) problems encountered; solutions developed to solve problem areas; reliability of each technology; and mass and visible emissions performance. This comparative study draws on in-depth discussions with coke plant operators, assimilation of existing technical literature into summary comparisons, and compilation of existing emissions performance and other data available from regulatory agencies throughout the country.

The paper provides study results obtained to date. Analysis of sheds and mobile scrubber cars has been completed. However, assessment of operating experience with fixed-duct systems is still in progress.

PUSH CONTROL SYSTEM POPULATION: PAST, PRESENT AND FUTURE

Figure 1 compares the rate of installation for push controls to the total number of operating batteries, by year. Operating batteries were defined as all batteries scheduled for service in the mid-1980s, including those on hot idle due to poor business conditions. All domestic foundry and furnace coke producers are included in the totals. These data reflect an updating of GCA's 1981 inventory of steel mill pollution control equipment to mid-1983 (2).

The number of batteries controlled by each push system type appears in Figure 2. Comparison with 1980 data shows the renaissance of sheds, continued use of fixed-duct systems, and the decline of mobile scrubber systems for new installations.

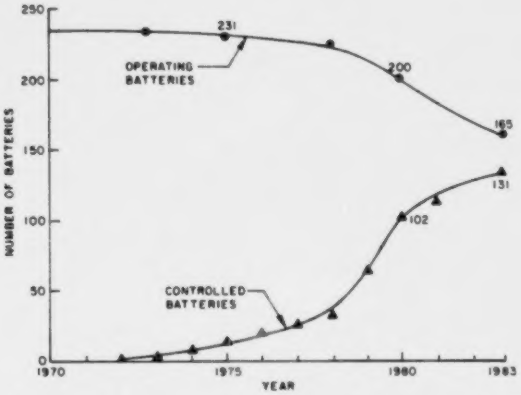

Figure 1. Number of Operating and Controlled Batteries in U.S.

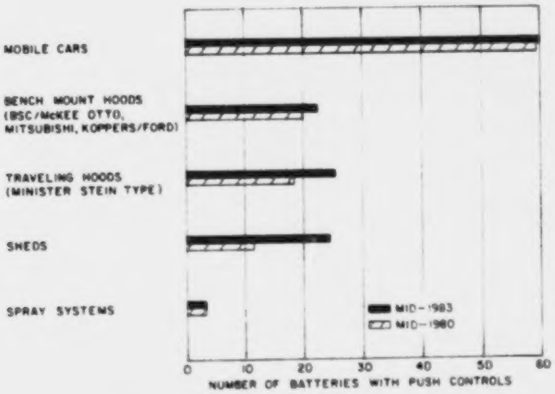

Figure 2. Distribution of Push Control Systems in 1980 and 1983.

A current listing of all installed push controls may be obtained by adding four systems to a list of installed and on-order systems provided previously in a 1981 paper (3), as follows: sheds at Wheeling Pittsburgh Steel, Follansbee, WV batteries 1, 2, 3, (8/82) and U.S. Steel, Clairton battery B (1982); National Engineers' fixed duct/traveling hood at Armco, Middletown, OH (12/82); and a Hawley fixed duct/traveling hood system recently sold to J&L Steel, Aliquippa, PA Works. The Hawley system is reportedly the only push control system sold in 1983 to date (9/83). No mobile scrubber cars have entered service since 1981 and it is not anticipated that any new systems of this type will be sold.

The vendors of all currently installed systems noted that no new systems are currently under development. However, virtually all existing designs have been continually refined and updated to decrease capital and O&M costs, and to improve system reliability.

PUSH CONTROL SYSTEM STATUS

Table 1 provides a quick comparison of currently-installed push control systems based on exhaust flowrate requirements and ability to control quench car travel emissions. An update of the status of mobile scrubber cars, sheds, and Minister Stein-type systems appears below.

TABLE 1. FLOWRATES OF TYPICAL PUSH CONTROL SYSTEMS

	Battery size (m)	Exhaust flowrate acfm x 10^3	Travel emissions controlled?
Mobile scrubber cars	4-6	13-90	Yes
Minister Stein[a]	4-6	100-140	Optional
Mitsubishi[a]	4-6	100-180	No
Koppers (fixed-duct)[a]	4-6	100-110	No
BSC/McKee Otto[a,b]	6	120-150	No
Hawley[a]	4	100-150	Optional
Sheds			
Recent designs	3-4 6	200-300 400	Yes Yes
Older designs	3-4 6	150-300 200-300	Sometimes Sometimes

[a] Fixed-duct systems with land-based scrubbers or baghouses.

[b] System relies on a 60 second "dedusting" period after the push to reduce travel emissions.

OVERVIEW AND UPDATE ON SHEDS

Table 2 summarizes North American shed installations to date. About 70 percent of all sheds are of the Great Lakes Carbon type, marketed by MikroPul, Inc. under a license agreement. New designs by Koppers and National Engineers have also been built.

Historical Overview

Great Lakes Carbon (GLC) experimented with the first prototype shed spanning 20 ovens on the A battery at the St. Louis, MO plant in the early 1970s. The shed was subsequently extended over the entire battery in 1972 and exhausted to the quench tower. A gas cleaner was later installed. Development details of the GLC shed appear elsewhere (4,5,6). The GLC design was installed at a number of coke plants in the mid-1970s.

TABLE 2. CHRONOLOGY OF SHED INSTALLATIONS

Shed Design	Installation	Battery[a] No.	Date on-line	Battery size (m)	No. of ovens[b]	Gas[c] cleaner	10^3 acfm during push (main shed)[d]	10^3 acfm per ton pushed	Travel controlled (?)
GLC/Mikropul	GLC/St. Louis	A; B&C	1972&76	3	93	BH	300	27	No
	Armco/Houston	1,2	07/76	4	62	WESP	190	14	
	Dofasco[e]	1,2,3	04/76	4	105	WESP	200	15	No
	Stelco/Hilton Works[e]	6,7	1976	5	156	WESP	157	8	
	Republic/Chicago[f]	1	1976	4	75	WESP	150	12	Yes
	USS/Clairton	B	1983	6	75	BH	480	19	Yes
	USS/Fairless	1,2	1982	4	174	BH	200	21	Yes
	USS/Lorain	H,G	1982	4	59	BH	200	21	Yes
	USS/Lorain	I,J	1982	4	59	BH	230	24	Yes
	USS/Geneva	1,2	1982	4	126	BH	200	21	Yes
	USS/Geneva	3,4	1982	4	126	BH	200	21	Yes
	Wisconsin Steel[g]	4	10/76	4	45	WESP	200	12	Yes
Koppers, Inc.	Erie Coke	1,2	1980	4	23	BH	---	--	No
	Inland/E. Chic.	C	1974	6	56	VS	220	12	Partial[h]
	J&L/Aliquippa	A-5	1976	6	56	VS	200	10	Partial[h]
	Shenango	1	Future	4	--	BH	300	21	Partial[h]
U.S. Steel[i]	USS/Clairton	17	08/75	4	61	VS	180	16	No
National Engineers[j]	W-P/Follansbee	1,2,3	1982	3	98	BH	230	25	No
Bethlehem Steel[k]	BSC/Burns Harbor	1	07/74	6	82	--	300	13	No

[a] Batteries listed are controlled by a single gas cleaner.
[b] Total no. of ovens for batteries listed.
[c] Type of gas cleaner: WESP = wet electrostatic precipitator; BH = baghouse; VS = venturi scrubber.
[d] Flow listed is for primary shed only excluding secondary extensions.
[e] Modified GLC design.
[f] Battery and shed dismantled in 1979.
[g] Plant shutdown.
[h] Small gap between the shed and quench station.
[i] Simple "box" design without venturi throat or containment volume.
[j] Shed is compartmentalized with multiple dampers. Flow listed is for entire shed.
[k] Shed dismantled.

Shed construction halted after the first series of installations due primarily to concerns about worker exposure to coal pitch tar volatiles (CPTV) under the shed, and partially to the promise of lower costs by use of lower-flow mobile scrubber car and fixed-duct systems. However, measurements of coke-side worker exposure at several sheds showed little difference in worker exposure between batteries with and without sheds. In 1978, the U.S. Occupational Safety and Health Administration (OSHA) indicated that subsequent to their investigation, OSHA maintained a neutral position on worker exposure and did not find sheds either acceptable or unacceptable (7).
Also during the later 1970s, operating and maintenance experience with mobile scrubber systems showed lower than anticipated performance. These factors helped to regenerate interest in sheds, as described below.

MikroPul/GLC Sheds

MikroPul modified the 1972 GLC design by extending shed sidewalls closer to ground level. This modification minimized cross-wind interference, increased indraft velocity through shed openings, and increased gas cleaner inlet temperature. Wet ESPs were selected for the mid-1970s MikroPul/GLC sheds to meet regulatory requirements for Method 5 back-half condensibles in effect at that time. The Dofasco and Stelco sheds were based on the GLC technology but incorporated some changes including a modified venturi design (8,9).

The unique design feature of the original GLC shed has been retained in the most recent installations. As shown in Figure 3, a narrow venturi section located at shed mid-height accelerates the push plume away from the bench and into an upper shed containment zone for eventual evacuation to the gas cleaner. A heat shield extending over the bench serves as one side of the venturi and also protects shed panels from direct heat. Heavy particulate not held aloft by the accelerating gas stream and the thermal buoyancy drop to the ground along the quench car tracks. The current design is described below.

In 1980, U.S. Steel contracted MikroPul to design and install eleven new MikroPul/GLC sheds with baghouses at four plant locations. The basic venturi design from the earlier GLC sheds was retained, with the following modifications.

- Secondary sheds to bridge gaps between battery pairs, and between the end battery and quench tower. This controls travel emissions and reduces escape from shed ends.
- Inspection doors on shed sides allow for conduct of coke-side door leak inspections.
- Manually-operated vacuum cleaning devices fitted to shed interiors for deflection plate (heat shield/baffle) cleaning.
- Improved flashing and sealing to reduce emission escape.
- Increased exhaust flowrate.

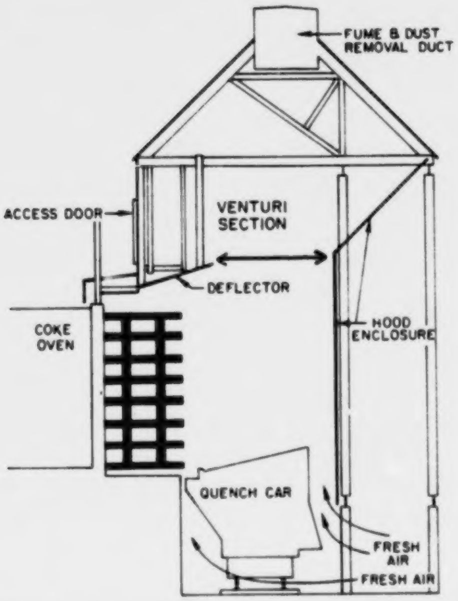
FUME & DUST REMOVAL DUCT
ACCESS DOOR
VENTURI SECTION
DEFLECTOR
COKE OVEN
HOOD ENCLOSURE
QUENCH CAR
FRESH AIR
FRESH AIR

Figure 3. Cross-Section of MikroPul/GLC Shed. U.S. Patent No. 3,844,901

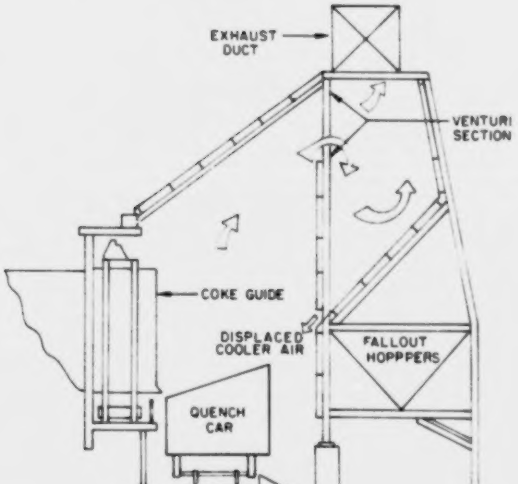
EXHAUST DUCT
VENTURI SECTION
COKE GUIDE
DISPLACED COOLER AIR
FALLOUT HOPPPERS
QUENCH CAR
WHARF

Figure 4. Koppers New Shed Design.

Like the older MikroPul/GLC sheds, the new designs use carbon steel structural members which cantilever the shed over the battery coke side so no additional weight rests on the battery. As before, stainless steel, corrugated panel sheeting is used. The sheeting is placed on the inside of the side-wall framework to help reduce particulate build up. MikroPul indicated the sheds could be built with precast concrete, reducing capital costs about 20 percent.

MikroPul also offers the MikroPul/Patton coke shed, which has been described previously (10,11). No sheds of this type have been sold to date. The design diverts the push plume into a containment section located behind the quench car. Heavy particulate falls into dust hoppers, while multiple baghouses mounted on the shed side clean captured emissions. The approach claims to reduce capital investment for ductwork, and to reduce energy requirements for air movement.

Koppers Shed Designs

Two Koppers sheds constructed at new 6-m batteries in 1974 and 1976 are similar to the GLC design, but with a less pronounced venturi effect. The two sheds are nearly identical with single 200,000 to 220,000 acfm scrubbers (ΔP of $\sim$30 inches H_2O). Both batteries use preheated coal which generally produces well-coked pushes. The Inland shed is clad with carbon steel panels, while the J&L shed uses stainless steel as is more common.

Koppers recently installed a new shed design at Shenango's new No. 1 battery. However, the battery has not entered service due to low coke demand. The latest Koppers design, shown in Figure 4, uses a horizontal flow venturi instead of the vertical flow MikroPul/GLC design. The Koppers patent claims the approach will minimize coke fallout on workers compared to both the original GLC design and the curved roof section of the MikroPul/Patton concept. The Koppers patent also claims lower horsepower requirements, longer bag life, reduced gas cleaner loading, and reduced cleaning of shed interior (12).

National Engineers Associates Shed

The National Engineers shed, shown in Figure 5, has several vertical partition walls in the upper plume containment zone to restrict horizontal plume movement. Offtake ducts with isolation dampers direct exhaust flow to

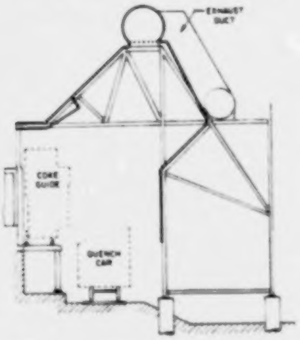

Figure 5. National Engineer's Shed.

shed sections above a push. The patent claims effective control of a 4-m battery with less than 200,000 acfm (13). The only installation to date entered service in 1982 at Wheeling Pittsburgh Steel's Follansbee, WV plant.

Older Shed Designs

The U.S. Steel, Clairton shed on battery No. 17 is essentially a box-type design with an outwardly-sloping back wall located close to the quench car. This older installation is about two-thirds as tall as modern designs for 4-m batteries, has a lower exhaust flowrate and lacks a venturi section and upper plume containment zone.

The Bethlehem Steel, Burns Harbor shed on Battery No. 1 which was not of the MikroPul/GLC design, was dismantled in the mid-1970s and replaced with a fixed-duct system. This was much publicized as an example of poor working conditions rendering shed technology unacceptable. EPA studies of the Burns Harbor shed noted that green pushes during a rapid push cycle overwhelmed shed exhaust capacity resulting in heavy plume density inside the shed, and substantial emissions leakage. The Burns Harbor shed did have an upper plume containment section much like the GLC design, but lacked a comparable venturi section for gas stream acceleration and minimization of particulate fallout (14,15).

UPDATE ON MOBILE SCRUBBER CARS

Table 3 lists currently-installed mobile scrubber cars by car type, and the exhaust flowrates provided by each design. Almost one-half of the 47 cars installed to date are of the Chemico Halcon (H-II and H-III) design. The Chemico cars use a high-pressure hot water nozzle arrangement to exhaust and clean push emissions from the coke guide hood and enclosed single-spot quench car. The H-II system uses an on-board hot water heater and on-board electricity generation for motive power and scrubber pumps. The H-III relies

TABLE 3. MOBILE SCRUBBER CARS AND EXHAUST FLOWRATES

Car type	Number of cars installed	Battery size, (m)	Push exhaust flow, scfm
Chemico H-II, H-III	21	4,5	90,000[a]
Granite City	8	4	42,000
Koppers	10	4-6	13,500 - 30,000
U.S. Steel	5	6	65,000 - 80,000
Lone Star/Koppers	1	5	55,000
Dravo	1	6	30,000
Two-Step-Quench	1	4	4,600

[a] 90,000 scfm maximum available for green push (flow is temperature-controlled).

on a land-based hot water heater with a high pressure transfer arm to supply the car while at the quench station. The H-III has no on-board electricity generation capability since power is drawn from conventional hot rails. The H-II was based on prototype installations at Interlake in 1973-74; the H-III was designed and installed in the mid to late 1970s without benefit of a first generation prototype. Although the basic design of all H-II and H-III cars is essentially identical, numerous minor differences in certain car system layouts of each type are evident. The first Chemico car was sold to J&L in early 1976, and the last order was in 1979. In January 1980, Envirotech/Chemico announced they were withdrawing from the mobile scrubber car business.

Of the ten Koppers cars installed since 1973, seven remain in service. Although specific installations varied somewhat in design (flowrates, single-spot versus conventional quench cars), all Koppers cars use conventional wet scrubbers and exhaust fans. The Granite City cars, developed by National Steel at the Granite City plant, were of a similar design concept. Based on experience with the first generation system, the cars were redesigned to improve reliability and maintainability and sold to three other coke plants. The two-step-quench (TSQ), the Koppers/Lone Star and Dravo mobile scrubber cars each have a single U.S. installation.

OVERVIEW AND UPDATE OF MINISTER STEIN SYSTEMS

The first Minister Stein system in West Germany was based on the experience developed by Hartung, Kuhn & Company (HKC) during installation of 20 hood-type push controls between 1964 and 1974 in Europe, Australia and Japan. The original system, at the Minister Stein coking plant of Ruhrkohle, AG in Dortmund, West Germany, showed an availability of 98 percent between 1975 and 1977 (16). Compared to other fixed-duct systems available at that time, the Minister Stein featured a lower cost, lower maintenance connection between the hood and exhaust duct via a continuous belt tripper device, and a heat exchanger to reduce gas temperature and volume upstream of the exhaust duct. This approach eliminated the maintenance intensive doors, lids and actuating mechanisms required by existing fixed-duct systems. The heat exchanger was cooled by operating the exhaust fan at close to full load during non-push periods.

Table 4 summarizes North American installations of the Minister Stein system plus two additional systems which also use the continuous tripper belt concept. The first North American installation at Dofasco in 1978 modified the original Minister Stein to control travel emissions by extending ductwork to the quench tower and constructing the collection hood independent of the coke guide. The first U.S. installation, also in 1978, at Allied Chemical's No. 4 battery in Ashland, KY (now owned by Armco) also included travel emissions (17).

The 1980 Minister Stein installation at Armco/Ashland's No. 3 battery represented the first new generation Minister Stein which features reduced weight and cost. The Ashland installation includes a guarantee from Dravo for

TABLE 4. CHRONOLOGY OF MINISTER-STEIN TYPE INSTALLATIONS

Plant/location	Date on-line	Battery No.	Battery height, (m)	Gas cleaner	Exhaust flowrate, scfm	Travel emissions controlled?
Dofasco	08/78		6	Scrubber	140,000	Yes
Armco/Ashland, KY	10/78	4	5	Scrubber	100,000	Yes
Detroit Coke, MI[a]	11/79	4	5	Baghouse	120,000	Yes
Interlake, Chicago, IL	1979	1,2	4	Scrubber	100,000	Yes
Citizens Gas, Indianapolis, IN[a]	12/79	1	5	Baghouse	120,000	Yes
Armco/Ashland, KY	11/80	3	4	Scrubber (existing)	110,000	No
J&L/Pittsburgh, PA	09/81	P1-P4	4	Baghouse	125,000	
Armco/Middletown, OH[b,c]	1983	2	4	Baghouse	120,000	
Wheeling Pittsburgh[c,d]	1980	1,2	4	Baghouse	110,000	

[a] Foundry coke plant.

[b] National Engineers design.

[c] Last two installations not Dravo/Minister Stein, but are similar systems. All other plants use Dravo's Minister Stein.

[d] Baumco design by Pennsylvania Engineering.

an on-line reliability exceeding 90 percent for a 3 to 4 month period. The specific modifications at Ashland and subsequent installations include the following:

- Decreased hood weight via lighter construction and removal of the heat exchanger;
- Conversion of a two-section hood to a single section;
- Use of hydraulic braking instead of the original counterweight system;
- Use of square, self-supporting ductwork instead of the original circular duct with internal bracing.
- New design, telescoping damper flaps between hood and quench cars to replace original hydraulic flaps; and
- Single-spot quench car design using 20 ft. long hood.

Dravo noted that the Minister Stein design currently requires 1500-2000 HP for a scrubber and 800-1000 HP for a baghouse. Dravo reported a new West German system which is operating at 85 percent availability at 50 percent the cost of a Minister Stein. However, Dravo expressed doubts that the system could meet current U.S. emission standards.

PUSH CONTROL SYSTEM PROBLEM SUMMARY

Detailed studies of design and O&M problem areas are summarized below. Information regarding fixed-duct systems will be available when studies are complete later this year. More detail may be found in the reports on each system type.

In general, the harsh coke plant environment has contributed to many of the reported equipment problems. The deleterious effects of hot, corrosive gases and steam plumes are compounded by the 24-hr per day, heavy service duty required of all coke oven machinery. Additionally, several push control installations in the U.S. represent first generation systems which proved not fully capable of handling the severe environment.

MOBILE SCRUBBER CAR PROBLEMS REPORTED

Mobile scrubber cars have developed a reputation for frequent breakdowns and for requiring a high level of both scheduled and unscheduled maintenance. Throughout the mobile scrubber car study, several recurring themes become evident regardless of system design or manufacturer, as follows.

- Many coke plants did not initially have the technical expertise to quickly troubleshoot car problems.

- Preventative maintenance programs often were not implemented with enough rigor to prevent breakdowns.

- Many cars were not originally designed and/or built to withstand heavy service duty, and to facilitate quick and easy repair when breakdowns occurred.

To improve car performance, many companies established rigorous maintenance programs to re-engineer unreliable car systems, and to redesign car layout to simplify and speed repairs. These programs are very labor intensive and expensive, and represent a considerably greater level of effort compared to maintenance of larry cars, pushers, and door machines. Highlights of the mobile scrubber car study appear below; greater detail is available in the existing report, and in reports currently under preparation (18).

Chemico H-II and H-III Cars

The study of the 21 Chemico cars, completed in mid-1982, found that many problems which reduced car availability were either solved, or being brought under control as plants gained operating experience. However, several major problems affecting car availability were reported by steel companies as only partially, or temporarily solved. Several companies noted that as existing problems are solved, and the cars operated longer, new problems were expected as equipment ages and wears. Four of the five steel companies operating these systems were visited; each company indicated they found the car systems inherently difficult to maintain due to equipment complexity and severe service conditions inherent at coke batteries.

The equipment vendor noted that the technology and equipment used on the H-II and H-III cars are not complex relative to other steel mill machinery, but are complex compared to the relatively unsophisticated process equipment at most coke plants. The vendor felt the major problem affecting car availability was a lack of technical expertise at many plants to effectively maintain the systems.

Problem areas restricting continuous service of Chemico cars were reported for the scrubber car, the land-based hot water heating and transfer station (H-III only) and the coke guide/single spot quench car. Numerous problems were reported by the steel companies, and although serious in nature, most had been solved. Frequently-reported problems with the land-based hot water heating and transfer station included the following, although a large number of additional problems were also reported by one or more plants:

- Poor coke oven gas combustion in the land-based hot water heater;

- Heater system control malfunction;

- Scrubber water treatment system malfunction; and

- Hot water transfer (to H-car) failure.

Transfer arm failures, Femco (process control communication) problems, and water treatment problems were still affecting availability at some plants in mid-1982. Most other problems were either solved, or solutions were reportedly developed.

Three continuing problems with the single-spot quench car and coke guide hood were reported as not completely solved, as follows:

- Coke spillage during push;
- Track and bed deterioration, causing car rocking, potential derailment, and collisions; and
- Coke box warpage.

Numerous other quench car and coke guide problems reported by the mills substantially reduced car availability during start-up and shakedown periods, but were reported to be either solved or under control.

A variety of problems with the scrubber car itself were commonly reported, although most were solved with considerable effort during start-up and break-in periods. Remaining problems include traction drive motor wear, Femco (process control) communication difficulty, and excessive deterioration of ductwork and seals.

Plants without a spare car generally performed routine maintenance during one 8-hr shift per week. Plants with a spare car either ran a car until a disabling breakdown occurred, or followed an established schedule for alternating cars. Maintenance facilities ranged from outdoor, unprotected rail sidings at several plants, to a fully-enclosed, dedicated car repair shop at others.

Maintenance crews ranged from a small group who assisted in car start-up and continued to service the units, to a situation where several maintenance personnel frequently rotated in and out of the car repair crew. A commonly-reported maintenance requirement for a high availability was a foreman or supervisor with primary responsibility to keep the car(s) running, and full support of plant engineering, maintenance and management.

Other Mobile Scrubber Cars

Except for the Lone Star/Koppers car, all non-Chemico mobile scrubber cars rely on conventional wet scrubbers and on-board exhaust fans. Both the Koppers and Granite City cars underwent substantial redesign effort to improve availability and ease of maintenance based on experience with first generation systems. Plants showing relatively high availability for these systems report high maintenance and frequent replacement of almost all car parts including scrubber components and even car frames. The Granite City and Koppers cars do not use the programmable logic circuits used in the Chemico designs, and are based on conventional equipment operations which are more easily repaired by coke plant operators. Maintenance requirements for some of the Granite City cars have been reported as about one man, full-time, each day.

First generation Koppers cars encountered several serious problem areas that severly limited car performance. Later designs, however, are operating much more satisfactorily. The first-generation Granite City car at Granite City Steel formed the basis for subsequent designs sold to other companies. The Granite City installation has subsequently been upgraded to include the second generation changes.

SHED PROBLEM AREAS REPORTED

Compared to mobile scrubber cars, the list of O&M problem areas is relatively short for sheds. Corrosion of scrubbers and wet ESP internals encountered in early shed designs were largely overcome by more attentive pH control and use of stainless steel in critical areas. Particulate fallout inside sheds is reduced with the venturi-section concept compared to the box-type design. Worker exposure to CPTV under sheds has been shown comparable to exposure without sheds (7,8,9). Excessive escape of emissions from underneath side walls and through shed ends has been reduced by (a) extending the shed beyond the last oven; (b) use of secondary, evacuated sheds, or tunnels between sheds on a battery pair; and (c) shed extensions to the quench tower for travel emissions.

Several problems have been encountered during initial operation of recent sheds. Extensions to quench towers have, in several instances, allowed quench tower steam to enter the baghouse, causing freezing of bags and baghouse cleaning mechanisms in winter. This situation has been resolved by improved insulation on key baghouse components and by removing select panels on the secondary shed extensions to allow escape of quench steam.

Maintaining leak-free seals between shed panels, side walls and roof sections, access door panels, and the joint with the battery topsides requires frequent attention. Neoprene and other rubber seals have proven easily deteriorated. One plant reported success with use of refractory material to keep panel joints leak-free. Additional sheet-metal flashing and caulking is the usual solution. Deterioration and corrosion of the shed cladding (side-walls, roof) itself have not proven a serious problem since most sheds were covered with stainless steel sheeting.

Blinded bags from hydrocarbon deposits have been reported for several shed installations where the initial lime precoat was not used or was interrupted. A few plants, however, operate without a lime precoat. Some problems have been reported with maintaining desired exhaust flowrates between a pair of sheds connected to a common baghouse due to damper and control equipment malfunction. These problems have been corrected by new equipment or maintaining constant shed exhaust rates.

AVAILABILITY DATA

Availability data compiled to-date during the study appear in Table 5, including the time frame covered, and whether spare mobile cars were available. Data with specific dates listed were compiled from daily or weekly

TABLE 5. AVAILABILITY DATA COMPILED TO DATE FOR PUSH CONTROLS[a]

System	Plant and location	Average monthly availability reported (%)	Period covered	Comments
Mobile Scrubber Cars				
Chemico H-III	USS/Clairton (bat. 1-3)	34	02/81-03/82	6 cars serve 5 battery units
	USS/Clairton (bat. 7-9)	25	01/81-03/82	
	USS/Clairton (bat. 15)	54	01/81-12/81	
	USS/Clairton (bat. 19-22)	42	01/81-03/82	
	USS/Clairton (bat. 7)	82	05/83-06/83	
	J&L/IHW (bat. H-9)	16	04/81-06/81	No spare car
	J&L/IHW (bat. H-4)	17	04/81-09/81	No spare car
	Republic/Warren	82	05/81-02/82	One spare car
Chemico H-II	BSC/Bethlehem	85	01/80-12/80	No spare car
	Shenango	80	09/80-11/81	No spare car
		67	07/82-10/82	No spare car
		65	01/83-04/83	No spare car
	J&L/Pittsburgh	18	12/79-03/81	No spare car
	BSC/Sparrows Point	55	10/82-12/82	No spare car
Granite City Car	NSC/Granite City	85	Unknown	One spare car
		95	Summer 1982	One spare car
	Inland	35	Unknown	3 cars/5 batteries
	Armco/Hamilton	70	Unknown	No spare car
Koppers Car	RSC/Cleveland, OH	94	Unknown	One spare car
	Koppers/Woodward, AL	90	02/81-09/82	2 cars/2 batteries
	NSC/Weirton	10	Mid-1970's	No spare car
	Inland	39	Unknown	No spare car
Fixed-Duct/Land Base				
Mitsubishi	USS/Gary	99.8	4 months	System A
		97	1 year	System B
Minister-Stein	Minister Stein, W. Germany	98.4	1975-1977	
	J&L/Pittsburgh	89	08/82-07/83	
	Dofasco	99	Annual average	
	Interlake	60-70	11/80-12/81	
		99	1/82-3/82	
	Unknown	97	Unknown	Recent Dravo data
Sheds				
Koppers	J&L, Aliquippa, PA	>90	1983	
MikroPul	USS Fairless, Clairton	80-100	1983	Monthly range

[a] Data represent currently-available information, not a thorough industry-wide compilation.

operating logs and therefore represent the most reliable information. These data represent the number of controlled pushes versus total pushes on a 24-hr per day basis.

Data shown without specific dates represent verbal estimates by steel companies, vendors or regulatory agencies, and are less reliable due to weak documentation. More detailed information is currently being solicited.

The availability data must be viewed primarily as a historical representation and not necessarily an indication of what availability could be achieved. For example, the average availability for the Clairton Chemico cars prior to the 1982 shutdown show relatively low averages. However, the average values mask the trend of improved availability which resulted from U.S. Steel's concentrated effort to re-engineer car systems to improve reliability. For each of the six Clairton Chemico cars, the best month averaged about 80 percent prior to the 1982 shutdown, and also for the one car recently brought on-line.

COST DATA

Installed capital cost data compiled for each control system type appear in Table 6. All data were updated to reflect mid-1983 dollars by an appropriate equipment cost index. The data represent typical costs for new installations provided by the equipment vendors except for the Mitsubishi data which represent three recent installations. The cost data are provided as a guideline; equipment vendors are quick to note that capital costs are very site specific. The primary variable influencing cost estimates is the degree of battery modification and new equipment required. Modifications required at some plants, but not others include quench car track upgrading, new quench cars, extensive bench or coke guide modifications, new utility services, relocating of interferring structures, new quench locomotive, extensive foundation work, and so on.

MikroPul noted that their bids on future shed installations would be lower than recent installations due primarily to reduced engineering costs and depressed market conditions for steel and labor. Dravo reported the following items influence Minister Stein costs: construction material-stainless or carbon steel; requirement for travel control; new single spot or conventional car; sophistication of locomotive electronics; type of electrical hook-ups; type of drive system. Dravo indicated their 1983 bid prices are equivalent to 1978 costs due to redesign for weight reduction.

The low maintenance costs for recent shed installations reportedly offset the higher capital and operating costs associated with the high flow systems. Most modern shed designs call for two to three times more exhaust air than a fixed-duct system.

EMISSIONS TEST DATA

Mass and visible emissions test data are provided herein for almost one-half of all installed systems. All data compiled to date from federal and state regulatory agencies are included. When multiple stack tests were performed, the lowest results were selected, provided the tests were accepted by the regulatory agency. However, it was generally not possible to determine whether the mass or VE data represent typical performance, or simply the performance only during the test program. Compounding this limitation is a frequent lack of process data to describe coking time, flue conditions, and presence of green coke.

TABLE 6. VENDOR ESTIMATES OF INSTALLED CAPITAL COSTS FOR PUSH CONTROLS IN MID 1983 DOLLARS[a]

System	No. of batteries[b]	Battery size (m)	System cost, 2nd-qtr. 1983, million $	Comments
Mobile Scrubber Cars				
Chemico H-II	1-3	4-6	5-6	Vendor quote (1979)
Chemico H-III	1-3	4-6	5.5-6.5	Vendor quote (1979)
Granite City Car	1-3	4	4.6	Vendor estimate (1982)
Sheds				
MikroPul/GLC				(MikroPul 1983 quotes)
recent	2 (2 sheds)	3-4	9-10	Steel, including design costs
future	2 (2 sheds)	4	4-5	Steel
			3-4	Concrete
MikroPul/Patton	2 (2 sheds)	4	~5	Steel
National Steel	1	4	5	Vendor estimate
Fixed-Duct Systems				
Dravo "Minister Stein"	1-2	-	7-10	Dravo estimate (1983)
Mitsubishi	1-2	-	9.5	$6.7 mil (1979) for system plus $2.8 mil for battery modifications
	2	4	6.5-7.5	Estimate
Hawley	1-2	4	2.5-5.1	Vendor quote (1979)

[a] All data updated to mid-1983 dollar values. Dates of original estimates used for updating appear in comments column.

[b] Single systems can handle range of batteries shown.

MASS EMISSIONS DATA

Table 7 summarizes mass compliance test data for 48 push control systems, showing both outlet concentrations and pounds per hour. The data include the average of all tests for a particular system type, and also the range of values for individual systems. All data are front-half catch only, based on EPA Method 5 modified as necessary for the intermittent push cycle.

The mass test data for mobile scrubber cars and sheds represent emissions measured during the push and travel periods. However, the fixed-duct measurements include travel emissions only if the particular system tested controls travel emissions.

The modification of Method 5 to handle the intermittent push cycles is an important factor to consider in evaluating mass test data. The mobile scrubber car data are probably the most consistent, in that all measurements started with the initiation of push ram movement, and terminated when quench sprays were activated. The only major differences are in number of traverse points which ranged from 16 to 48 (usually equivalent to number of pushes sampled since one traverse point is normally applied to each push).

The shed and fixed duct data, however, are based on slightly different measurement techniques. Sample time for these systems ranged from 0.7 to 6.0 minutes per push. Although field test crews probably sampled until most emissions had cleared the hoods and the gas cleaner, firm documentation is often unavailable.

VISIBLE EMISSIONS DATA

Table 8 compares visible emissions (VE) data compiled for approximately 58 different push control systems based on EPA Method 9 and Method D observations. The Method D data represent the number of seconds during the push during which VE escaping hood capture equalled or exceeded 20 percent opacity. The number of pushes observed, and the number of plants evaluated are also shown.

The VE data in Table 8 describe the push period only, i.e., from start of ram movement until the quench car began movement to the quench tower. The one exception are the data for the National Engineers shed which include travel emissions. Most VE observations were recorded at or above the battery top-side level, using the sky or collector main as a contrasting background.

TABLE 7. MASS COMPLIANCE TEST SUMMARY

	No. of Systems Tested	gr/dscf		lb/hr	
		Range	Average	Range	Average
Scrubber Gas Cleaner					
Mobile Cars:					
Chemico H-III	8	0.012-0.065	0.025	NA	NA
Chemico H-II	2	0.013-0.025	0.019	7.4-19	13
Granite City	5	0.019-0.041	0.032	7.3-16	12
USSC	3	0.027-0.20	0.098	10-96	46
Koppers	3	0.020-0.048	0.031	5.0-7.4	5.9
Lone Star	1	---	0.008	NA	NA
Fixed-Duct Hoods:					
Mitsubishi	2	0.015-0.042	0.029	21-36	29
Otto-McKee	3	0.010-0.017	0.014	11-20	17
Koppers/Ford	3	0.006-0.022	0.012	5.2-17	9.2
Dravo-Still	2	0.005-0.007	0.006	4.5-5.7	5.1
Hawley	1	---	0.0044	--	3.77
Sheds:					
Koppers	2	0.004-0.006	0.005	6.9-11	9.0
USSC	1	---	0.027	--	42
Baghouse Gas Cleaner					
Fixed-Duct Hoods:					
Mitsubishi	3	0.004-0.009	0.006	3.7-12	7.3
Otto-McKee	1	---	0.014	--	17
Hawley	3	0.002-0.005	0.003	2.0-5.0	3.1
PECOR	1	---	0.004	--	4.1
National	1	---	0.001	--	1.2
Sheds:					
New MikroPul	2	0.001-0.004	0.003	1.9-6.8	4.4
Old MikroPul	1	---	0.002	--	4.9

NA = Flow rate not available to calculate lb/hr.

TABLE 8. VISIBLE EMISSIONS DATA SUMMARY

	No. of Systems	No. of Pushes	Avg. Sec./Push ≥20% (Method D)	No. of Systems	No. of Pushes	Avg. No. EPA Method 9 VEO/Push ≥20%
Mobile Cars						
Chemico H-II	4	401	7	0	0	-
Chemico H-III	2	158	17	3	218	0.6
Koppers Erikar	1	6	34	0	0	-
U.S. Steel	1	42	45	1	131	1.9
Granite City	1	40	14	1	106	1.0
Koppers 1-spot	3	59	17	2	41	
Total	12	706	avg. 13[a]	7	496	avg. 1.1[a]
Bench-Mount Hoods						
Mitsubishi	0	0	-	5	325	0.6
Otto-Mckee	1	60	15	2	50	2.3
Koppers/Ford	0	0	-	3	165	0.7
Total	1	60	avg. 15	10	540	avg. 0.8
Traveling Hoods						
Dravo-Still	0	0	-	2	53	0.2
PECOR	1	39	0	0	0	-
Total	1	39	avg. 0	2	53	avg. 0.2
SHEDS						
New MikroPul	2	32	21	2	75	0.3
Old MikroPul	0	0	-	1	1	3
Koppers	1	25	5	0	0	-
National	1	27	1	1	27	0.04
Total	4	83	avg. 10	4	103	avg. 0.2

[a] All average values weighted by number of pushes.

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COST/BENEFIT OF FUGITIVE EMISSIONS CONTROLS FOR TSP AND POSSIBLE PM10 COMPLIANCE

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ABSTRACT

Alternative controls of fugitive emissions from blast furnaces, basic oxygen furnaces, unpaved roads and paved roads were examined for costs and resultant air quality improvements. Fugitive emissions from a representative steel facility based on a composite of ten integrated steel plants were analyzed for their impacts on the ambient air quality. The Industrial Source Complex (ISCLT) model was used to predict total suspended particulates (TSP) and particulate matter with a 10 micron cutoff (PM10) concentrations. Impacts were determined at set distances downwind of the plant. Emissions characteristics were derived from field testing and published emission factors.

Reasonably Available Control Technology (RACT) and alternate control technologies were analyzed for their effects on ambient air quality. The effect of the control technologies on fugitive emissions strength and particle size were accounted for in the modeled impacts of TSP and PM10 concentrations at various distances from the plant.

The cost function of the control technologies were analyzed on a dollars per $\Delta \mu g/m^3$ improvement of air quality based for TSP and PM10. Capital and operating costs were included in defining the cost function. Controls on roads were found to be significantly more cost effective in improving air quality than additional controls on blast furnaces and basic oxygen furnaces. Results from this analysis can lead to a more efficient utilization of money in complying with the current TSP standard and a proposed PM10 standard.

INTRODUCTION

The iron and steel industry in the United States has expended large sums of money in complying with air pollution control requirements under State Implementation Plans (SIPs). These expenditures have been focused primarily on reducing particulate matter emissions through the installation of Reasonably Available Control Technology (RACT). In many cases, installation of RACT has not led to attainment of the National Ambient Air Quality Standards (NAAQS) for Total Suspended Particulates (TSP). This paper investigates the cost effectiveness of these controls on selected iron and steel sources and their corresponding effects on improving air quality. More stringent alternative controls are also investigated for their cost effectiveness in further improving air quality.

Control strategies for fugitive emissions from blast furnaces, basic oxygen furnaces (BOF) and unpaved and paved roads in a "typical" iron and steel facility are investigated. This plant is based on a BOF producing 3.2 million tons of steel per year, and three blast furnaces producing 2.5 million tons of hot metal per year to support the BOF. Roadway type, mileage and vehicle mix were derived from literature for unpaved and paved roads within a mill containing a BOF and blast furnaces. Control scenarios for the three source types were defined as follows:

Scenario #1

BOF	Furnace enclosure
Blast Furnaces	Fume suppression
Roadways	Chemical dust suppression Vacuum sweeping

Scenario #2

BOF	Building evacuation
Blast Furnaces	Building evacuation
Roadways	More frequent chemical dust suppression and vacuum sweeping

In this analysis, Scenario #1 is considered RACT because several states have approved these installations under SIP related Consent Decrees.

Air quality impacts resulting from installation of these control scenarios are compared to the corresponding costs for the technology. This is done for TSP impacts and for air quality impacts of particulate matter with a mass cutoff of 10 microns aerodynamic diameter (PM10).

METHODS

DESCRIPTION OF "TYPICAL" PLANT

Iron and steel production and vehicular traffic data were investigated from ten integrated iron and steel mills to determine a description of a "typical" mill. The "typical" mill used for this study has the following characteristics:

o Basic Oxygen Furnace - two vessels, top blown operation producing 3.2 million tons per year;[1]

- Blast Furnaces - three furnaces each supplying 833,000 tons of hot metal per year; and

- Vehicular traffic - 10 miles of plant roadways (7.5 miles unpaved, 2.5 miles paved), travelled for a total of 6,668 vehicle miles travelled per day (VMT/d) by automobiles and light duty trucks, 320 VMT/d by medium duty trucks, and 510 VMT/d by heavy duty trucks.[2]

The mill layout is shown in Figure 1.

PARTICULATE EMISSION RATES

Particulate emission rates were calculated using published emission factors. Secondary emissions from BOF operations were determined using the following factors:[1]

Hot metal transfer	0.179 lbs/ton steel
Hot metal charging	0.377 lbs/ton steel
Tapping	0.291 lbs/ton steel
Teeming	0.07 lbs/ton steel

Secondary emissions from blast furnaces were calculated using the emission factor of 0.6 lbs/ton hot metal.[3] This factor for casthouse emissions includes tap hole and trough emissions, as well as emissions from runners.

Fugitive emissions from vehicular traffic on unpaved roads and parking lots were determined by the emission factor:[3]

$$EF = 5.9 \left(\frac{s}{12} \right) \left(\frac{S}{30} \right) \left(\frac{W}{3} \right)^{0.7} \left(\frac{w}{4} \right)^{0.5} \left(\frac{d}{365} \right)$$

Where: EF = emission factor (lbs/veh-mile)
s = silt content of road surface (%)
S = average vehicle speed (MPH)
w = average number of wheels per vehicles
W = average vehicle weight (tons)
d = dry days per year

Similarly, the emission factor for paved roads is:

$$EF = 0.090 \, I \left(\frac{4}{n} \right) \left(\frac{s}{10} \right) \left(\frac{L}{1000} \right) \left(\frac{W}{3} \right)^{0.7}$$

Where: I = industrial road augmentation factor
n = number of travel lanes
L = surface dust loading on traveled portion of road

Input data for the emission factor equations are listed in Table 1.

PARTICULATE SIZE DISTRIBUTION

Particle size is an important variable in modeling ambient air impacts from different sources. Particle size distribution from each source was

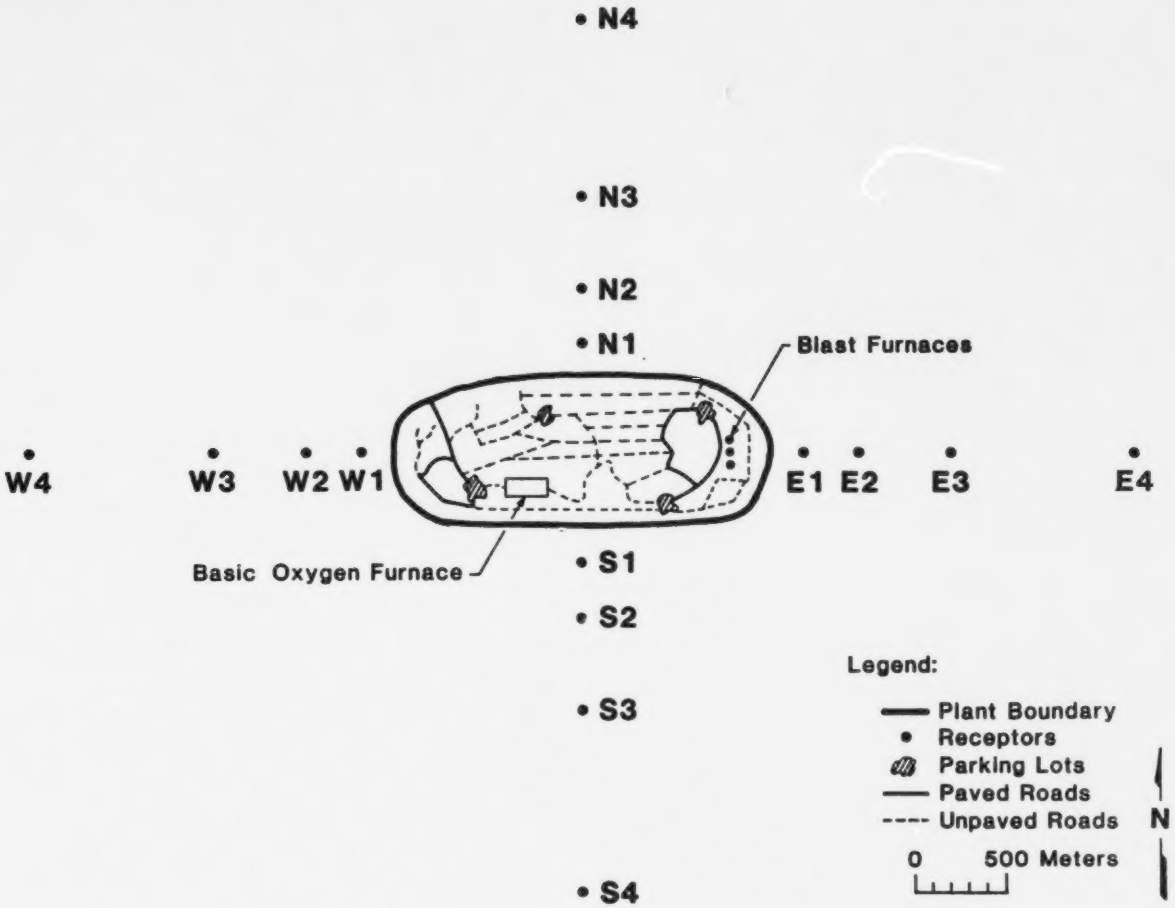
N4
N3
N2
N1
Blast Furnaces
W4
W3
W2
W1
E1
E2
E3
E4
Basic Oxygen Furnace
S1
S2
S3
S4
Legend:
Plant Boundary
Receptors
Parking Lots
Paved Roads
Unpaved Roads
0 500 Meters
N

Figure 1. Iron and Steel Facility with Air Quality Receptor Indicated.

TABLE 1. INPUT PARAMETERS USED FOR VEHICULAR TRAFFIC EMISSION EQUATIONS

Input Parameters	Values
Silt content of aggregate on road surface material	10.5% paved roads[2] 12.7% unpaved roads
Average vehicle speed on roads and parking lots	Variable (10-20 mph)
Average vehicle weight	A 2 tons[4] B 15 tons C 40 tons
Surface dust loading on traveled portion of road	3580 lbs/mile paved roads[2]
Number of dry days per year	212 days[5]
Number of active travel lanes	2 lanes
Industrial road augmentation factor	2.0
Average number of vehicle wheels	A 4 wheels[4] B 7 wheels C 11 wheels

determined using literature data and is classified by weight percentage into 8 particle diameter ranges in Table 2. All the sources concerned have a particle size distribution predominated by small particles, less than 15μ. Particle size distribution is affected by the control scenarios, but all uncaptured particles are assumed to be the same as uncontrolled.

MODELING

Impacts to ambient air quality were determined using the long term version of the Environmental Protection Agency (EPA) Industrial Source Complex (ISCLT) model. The model options used in this analysis were:

- Plume rise as a function of distance;
- Initial Sigma Z and Y;
- Gravitational settling and dry deposition particles; and
- Building and stack-tip downwash.

For this analysis, a constant wind speed of 4.3 m/s blew from all directions the same percentage of time. These assumptions were used to remove the meteorological bias from the results.

The emission inventory inputs to the model are listed in Table 3. Because the roads and parking lots are evenly distributed throughout the plant (Figure 1), the emissions from vehicular traffic were considered as area sources. Settling velocities were calculated by using equations 2-42 in the ISC manual. For iron-rich particles, a density of 5.7 gr/m^3 was used and for all others, 2.5 gr/m^3 was used.

The air quality impacts are modeled at receptors 0.2, 0.5, 1.0 and 2.0 km from the plant boundary in four directions (Figure 1). Modeled air quality impacts are also presented as average values for each receptor distance. Area-wide impacts are also presented by using a radii-weighted value to calculate the average impact over the 2-km radius.

COST OF CONTROLS

Capital and annual costs for each control scenario were determined from literature data and are listed in Table 4. Capital costs include the initial investment required to install and start up the control system. Annual costs include labor, maintenance, operation expenses for expendables and charges made to recover capital cost over the life of the system. For a direct comparison of costs, the capital cost is annualized over the life of the system and is included in the last line of Table 4.

RESULTS

AMBIENT AIR QUALITY IMPACTS

Ambient air impacts were determined by the ISCLT model described above. Because of the plant layout (Figure 1) and the assumed uniformity of wind speed and direction, the air quality impacts are influenced most by the height

TABLE 2. PARTICLE SIZE DISTRIBUTION

Aerodynamic Particle Diameter (microns)	Weight Percentage of Particles						
			Uncontrolled			Controlled	
	Blast Furnace[6]	BOF Secondary[7]	Paved Roads[8]	Unpaved Roads[8]	Baghouse[9]	Paved Roads[8]	Unpaved Roads[8]
0 - 5	21	74	21	22	100	34	18
5 -10	27	20	52	45	0	47	41
10-15	14	4	12	25	0	4	32
15-30	20	1.8	15	8	0	15	9
30-50	11	0.2	0	0	0	0	0
50-70	3	0	0	0	0	0	0
70-100	4	0	0	0	0	0	0
>100	0	0	0	0	0	0	0

TABLE 3. EMISSION INVENTORY FOR ISCLT MODEL

Scenario	Source Name	Source Type	Emission Rate (lbs/hr)	Emission Release Height (ft)
Uncontrolled	Blast Furnace	Volume	171.3	84.0
	BOF-Roof Monitor	Volume	336.1	150.0
	Unpaved Roads	Area	585.0	0.0
	Paved Roads	Area	111.0	0.0
Control 1	Blast Furnace	Volume	13.8	84.0
	BOF-Roof Monitor	Volume	34.9	150.0
	BOF-Baghouse	Stack	35.1	100.0
	Unpaved Roads	Area	117.0	0.0
	Paved Roads	Area	22.2	0.0
Control 2	Blast Furnace	Volume	5.1	84.0
	Blast Furnace-Baghouse	Stack	51.3	40.0
	BOF-Roof Monitor	Volume	8.4	150.0
	BOF-Baghouse	Volume	283.3	85.0
	Unpaved Roads	Area	29.2	0.0
	Paved Roads	Area	5.5	0.0

TABLE 4. ESTIMATED COSTS FOR CONTROL SCENARIOS ($ million)

	Basic Oxygen Furnace		Blast Furnaces		Vehicular Traffic	
	Scenario #1 (Furnace Enclosure)	Scenario #2 (Building Evacuation)	Scenario #1 (Suppression)	Scenario #2 (Building Evacuation)	Scenario #1 (Dust Control)	Scenario #2 (More Frequent Dust Control)
Capital Costs	12.560[1]	37.652[1]	3.750[10]	17.337[11]	0.089[13]	0.163[13]
Annual Costs	3.840[1]	11.930[1]	--[a]	4.881[11]	0.086[13]	0.190[13]
Annual Costs Including Annualized Capital Costs[b]	4.258	13.185	0.125	5.459	0.095	0.146

[a] Implementation of the suppression technology is considered to result in no incremental cost to maintain because of enhanced performance of the blast furnace[12]

[b] The amortization period for BOF and blast furnace control is 30 years and for road control it is 10 years.

and location of the source. Uncontrolled fugitive emissions and two control scenarios are investigated for each source - basic oxygen furnace, blast furnaces and vehicular traffic.

Basic Oxygen Furnace

Uncontrolled secondary emissions considered in this study are generated by hot metal transfer, charging, tapping and teeming. Primary emissions are controlled by a closed hood and scrubber. The total fugitive emissions rate emanating from the BOF roof monitor is 336.1 pounds per hour. This results in an ambient air impact of 17.7 μg/m³ for TSP and 16.4 μg/m³ for PM10 (Table 5) at the receptor nearest to the BOF (Receptor S1, Figure 1). Ambient air impacts diminish as a function of their distance away from the source.

The two control scenarios of secondary emissions from the BOF considered were furnace enclosure and complete building evacuation. In the first scenario, the furnace enclosure is equipped with hot metal transfer, charging and tapping hoods ventilated at a rate of 600,000 acfm to a baghouse that reduces emissions to 0.01 gr/dscf.[1] These emissions are discharged from a stack and have particle sizes less than 5μ.[9] The collection efficiency of the furnace enclosure is assumed to be 97 percent. One hundred percent capture efficiency is possible, but over an extended period is unlikely. The remaining uncaptured emissions and emissions from teeming are discharged from the roof monitor and assumed to have the same particle size distribution as uncontrolled. The total of secondary emissions from the stack and roof monitor is 70.0 pounds per hour.[1] The ambient air impacts of the stack and roof monitor emissions are highest at the receptor closest to the BOF, 2.7 μg/m³ for TSP and 2.6 μg/m³ for PM10 (Table 3). This reflects an improvement in TSP air quality of 15.0 μg/m³ at this receptor and an improvement in PM10 of 13.8 μg/m³. This control scenario results in an area-wide reduction in TSP by a factor of 6.3, and concurrent drop in PM10 by a factor of 5.9.

The control scenario of complete building evacuation will capture approximately 97 percent of the fugitive emissions[14]. The uncaptured secondary emissions escape through leak in the building. Controlled emissions are ducted to a baghouse to reduce emissions to 0.01 gr/dscf.[1] The evacuation for the whole building is 3.4 million acfm.[1] Since baghouses tend to produce relatively constant outlet concentrations, the emissions from the baghouse are dependent on flow. At a flow of 3.4 million acfm, the emissions would be greater than the furnace enclosure scenario. The total amount of emissions from the baghouse monitors and BOF roof monitor is 291.6 pounds per hour.[1]

Ambient air impacts of the building evacuation scenario are listed in Table 5. The receptor nearest to the BOF is affected most severely, 28.7 μg/m³ for TSP and 28.7 μg/m³ for PM10. The area-wide air quality is reduced by comparison to the uncontrolled scenario. This is the result of similar emission strengths (336.1 pounds per hour, uncontrolled; and 291.6 pounds per hour, controlled) and a lower emission height of the baghouse compared to the roof monitor.

TABLE 5. MODELED AMBIENT AIR QUALITY IMPACTS DUE TO BOF OPERATION

	TSP (μg/m³)			PM10 (μg/m³)		
Receptor	Uncontrolled	Control Scenario #1 (Enclosure)	Control Scenario #2 (Evacuation)	Uncontrolled	Control Scenario #1 (Enclosure)	Control Scenario #2 (Evacuation)
N1	10.8	1.5	15.5	10.0	1.5	15.5
N2	7.1	1.1	9.8	6.5	1.0	9.8
N3	4.6	0.8	5.9	4.3	0.7	5.9
N4	2.5	0.4	2.9	2.3	0.4	2.9
S1	17.7	2.7	28.7	16.4	2.6	28.7
S2	12.8	1.8	19.0	11.9	1.7	19.0
S3	6.4	1.0	8.7	6.0	1.0	8.7
S4	3.1	0.5	3.7	2.9	0.5	3.7
E1	5.0	0.8	6.5	4.7	0.8	6.5
E2	4.0	0.7	5.0	3.7	0.7	5.0
E3	2.9	0.5	3.5	2.7	0.5	3.5
E4	1.8	0.3	2.0	1.6	0.3	2.0
W1	9.0	1.3	13.1	8.4	1.2	13.1
W2	6.6	1.1	8.9	6.1	1.0	8.9
W3	4.3	0.8	5.5	4.0	0.7	5.5
W4	2.3	0.4	2.7	2.2	0.4	2.7
0.2 km	10.6	1.6	16.0	9.9	1.5	16.0
0.5 km	7.6	1.2	10.7	7.1	1.1	10.7
1.0 km	4.6	0.8	5.9	4.3	0.7	5.9
2.0 km	2.4	0.4	2.8	2.3	0.4	2.8
Area-wide Average	4.4	0.7	5.7	4.1	0.7	5.7

Blast Furnaces

Uncontrolled secondary emissions from the three blast furnaces escape from the casthouse monitors at a rate of 171.3 pounds per hour. The resultant air quality impacts are listed in Table 6. The highest TSP and PM10 impacts are on the receptor closest to the furnaces (Receptor E1, Figure 1). The other receptors have impacts related to their distance from the furnaces. (Note: The North and South receptors are equidistance from the blast furnace, therefore, they have the same impacts.)

Suppression of secondary emissions by a blanket of inert gas[10] was the first control scenario investigated. From opacity readings[10], the control efficiency was estimated to be 92 percent, resulting in a fugitive emission rate of 13.8 pounds per hour from the casthouses. Since this control technology does not involve fans, baghouses or stacks, the TSP and PM10 air quality impacts are directly proportional to the control efficiency (Table 6). Thus, this control scenario results in a 23.0 $\mu g/m^3$ and 11.7 $\mu g/m^3$ improvement of TSP and PM10 air quality, respectively at the closest receptor. Area-wide air quality is improved by a factor of 15.5 for TSP and a factor of 17 for PM10.

The second scenario is total evacuation. The capture efficiency of this system is not known, but it is not 100 percent.[6] For this study, the capture efficiency is assumed to be 97 percent. The uncaptured emission rate is 5.1 pounds per hour and has the same particle size distribution as the uncontrolled emissions. The capture emissions are vented into a baghouse at 300,000 acfm and through a stack. The efficiency of the baghouse, assumed as 67 percent from test results,[3] yields an emission rate of 54.9 pounds per hour. The total emissions from this scenario is 60.0 pounds per hour and results in a TSP air quality impact of 1.4 $\mu g/m^3$ and a PM10 impact of 1.3 $\mu g/m^3$ at the most severely affected receptor (Table 6). Overall air quality is incrementally degraded by a factor of 3.0 for TSP and 6.0 for PM10 when replacing the suppression technology with building evacuation. Interestingly, this scenario is better at reducing air quality impacts at the nearest receptor than scenario #1, but results in worse overall impacts.

Vehicular Traffic

Uncontrolled fugitive emissions from unpaved roads and parking lots are generated at a rate of 585.2 pounds per hour. Emissions from paved roads are produced at 111.2 pounds per hour. The total emission rate from all vehicular traffic is 696.4 pounds per hour results in a TSP impact of 65.6 $\mu g/m^3$ at the nearest North-South receptors (Receptors N1 and S1, Figure 1). Because the roads and parking lots are evenly distributed in the plant, and the wind was assumed to have an even distribution, the air quality impacts in the North are the same as in the South, and East is the same as in the West. The PM10 air quality impact is 50.3 $\mu g/m^3$ at the most severely affected receptors (Table 7).

The first control scenario is chemical dust suppression of unpaved roads and parking lots once every other month, and twice-a-week vacuum sweeping on paved roads. Control efficiency of these measures is 80 percent[4] and 65 percent[13], respectively. The particle size distribution changes slightly with

TABLE 6. MODELED AMBIENT AIR QUALITY IMPACTS DUE TO BLAST FURNACE OPERATION

	TSP (µg/m³)			PM10 (µg/m³)		
Receptor	**Uncontrolled**	**Control Scenario #1 (Suppression)**	**Control Scenario #2 (Evacuation)**	**Uncontrolled**	**Control Scenario #1 (Suppression)**	**Control Scenario #2 (Evacuation)**
N1	6.2	0.5	0.9	3.3	0.3	0.9
N2	4.8	0.4	0.8	2.5	0.2	0.8
N3	3.1	0.2	0.6	1.7	0.1	0.6
N4	1.5	0.1	0.4	0.8	0.1	0.4
S1	6.2	0.5	0.9	3.3	0.3	0.9
S2	4.8	0.4	0.8	2.5	0.2	0.8
S3	3.1	0.2	0.6	1.7	0.1	0.6
S4	1.5	0.1	0.4	0.8	0.1	0.4
E1	25.0	2.0	1.4	12.7	1.0	1.3
E2	11.8	0.9	1.0	6.1	0.5	1.0
E3	5.3	0.4	0.8	2.8	0.2	0.8
E4	2.0	0.2	0.5	1.1	0.1	0.5
W1	2.4	0.2	0.5	1.3	0.1	0.5
W2	1.9	0.1	0.4	1.0	0.1	0.4
W3	1.4	0.1	0.3	0.8	0.1	0.3
W4	0.8	0.1	0.2	0.5	0.0	0.2
0.2 km	10.0	0.8	0.9	5.3	0.4	0.9
0.5 km	5.8	0.5	0.8	3.0	0.3	0.8
1.0 km	3.2	0.2	0.6	1.8	0.1	0.6
2.0 km	1.5	0.1	0.4	0.8	0.1	0.4
Area-wide Average	3.1	0.2	0.6	1.7	0.1	0.6

TABLE 7. MODELED AMBIENT AIR QUALITY IMPACTS DUE TO VEHICULAR TRAFFIC

	TSP (µg/m³)			PM10 (µg/m³)		
Receptor	Uncontrolled	Control Scenario #1 (Dust Control)	Control Scenario #2 (More Frequent Dust Control)	Uncontrolled	Control Scenario #1 (Dust Control)	Control Scenario #2 (More Frequent Dust Control)
N1	65.6	13.1	3.3	50.3	8.6	2.2
N2	39.5	7.9	1.9	30.3	5.2	1.2
N3	22.3	4.4	1.1	17.0	3.0	0.7
N4	9.5	1.9	0.5	7.3	1.2	0.3
S1	65.6	13.1	3.3	50.3	8.6	2.2
S2	39.5	7.9	1.9	30.3	5.2	1.2
S3	22.3	4.4	1.1	17.0	3.0	0.7
S4	9.5	1.9	0.5	7.3	1.2	0.3
E1	45.6	9.1	2.3	34.9	7.0	1.6
E2	27.9	5.4	1.5	21.5	3.6	1.0
E3	16.1	3.2	0.8	12.3	2.1	0.5
E4	8.2	1.6	0.4	6.3	1.1	0.3
W1	45.6	9.1	2.3	34.9	7.0	1.6
W2	27.9	5.4	1.5	21.5	3.6	1.0
W3	16.1	3.2	0.8	12.3	2.1	0.5
W4	8.2	1.6	0.4	6.3	1.1	0.3
0.2 km	55.6	11.1	2.8	42.6	7.8	1.9
0.5 km	33.7	6.7	1.7	25.9	4.4	1.1
1.0 km	19.2	3.8	1.0	14.7	2.6	0.6
2.0 km	8.9	1.8	0.5	6.8	1.2	0.3
Area-wide Average	18.4	3.7	1.0	14.1	2.5	0.6

these controls.[8] With the control efficiency and particle size taken into account, the TSP air quality impact of the vehicular traffic is 13.1 μg/m³ at the nearest North-South receptor. PM10 impacts are reduced to 8.6 μg/m³. Area-wide air quality is improved by a factor of 5 for TSP and a factor of 5.7 for PM10 (Table 7).

The second control scenario involves a more frequent application of chemical suppressants (once a month) and a daily vacuum sweeping of paved roads. This strategy yields 90 percent control on unpaved roads and 95 percent control on paved roads.[13] The total fugitive emissions from vehicular traffic under this control is 75.2 pounds per hour. The TSP and PM10 air quality impacts are 3.3 μg/m³ and 2.2 μg/m³, respectively, at the most severely affected receptors. This is a 62.3 μg/m³ improvement in TSP air quality from the uncontrolled emissions at that receptor (Table 7). Overall air quality is incrementally improved by going from Scenario #1 to Scenario #2 by a factor of 3.8 for TSP and a factor of 4.1 for PM10 (Table 7).

COST/BENEFIT ANALYSIS OF CONTROLS

The cost/benefit of each control scenario is determined by the following equation:

$$C/B = \frac{\text{Annual Costs Including Annualized Capital Cost (\$ million)}}{\begin{array}{c}\text{Air Quality Impacts Uncontrolled -} \\ \text{Air Quality Impacts Controlled } (\Delta\mu g/m^3)\end{array}}$$

This analysis was done for the four receptors in the direction most affected by the source and the area-wide average air quality. The results of this analysis are in Table 8 and Table 9 for TSP and PM10, respectively.

Basic Oxygen Furnace

The control scenario involving furnace enclosure has a cost per μg/m³ TSP air quality improvement ranging from $0.284 million to $1.638 million for the directional receptors having the highest impact. The cost/benefit of this scenario, when considered for the whole area surrounding the plant, $1.151 million. The results are similar for PM10 air quality.

The second scenario, building evacuation, results in greater air quality impacts than the uncontrolled. This results in a negative cost benefit, specifically -$10.138 million for the area-wide average impact.

Blast Furnaces

The cost to control secondary blast furnaces emissions using the inert gas suppression system ranges from $0.005 million per μg/m³ TSP improvement to $0.069 million per μg/m³ for directional receptors. The cost per μg/m³ for PM10 is approximately double that for TSP. The cost per μg/m³ for TSP area air quality improvement is $0.043 million. The same PM10/TSP relationship holds for the area control.

TABLE 8. COST/BENEFIT OF CONTROL SCENARIOS FOR TSP AIR QUALITY ($ million/$\Delta\mu g/m^3$)

Receptor	Basic Oxygen Furnace		Blast Furnaces		Vehicular Traffic	
	Scenario #1 (Furnace Enclosure)	Scenario #2 (Building Evacuation)	Scenario #1 (Suppression)	Scenario #2 (Building Evacuation)	Scenario #1 (Dust Control)	Scenario #2 (More Frequent Dust Control)
Directional						
1	0.284	-1.464	0.005	0.231	0.002	0.002
2	0.387	-2.126	0.010	0.505	0.003	0.004
3	0.789	-5.730	0.026	1.213	0.005	0.006
4	1.638	-21.967	0.069	3.639	0.012	0.016
Area-wide Average	1.151	-10.138	0.043	2.184	0.006	0.008

TABLE 9. COST/BENEFIT OF CONTROL SCENARIOS FOR PM10 AIR QUALITY ($ million/$\Delta\mu g/m^3$)

Receptor	Basic Oxygen Furnace		Blast Furnaces		Vehicular Traffic	
	Scenario #1 (Furnace Enclosure)	Scenario #2 (Building Evacuation)	Scenario #1 (Suppression)	Scenario #2 (Building Evacuation)	Scenario #1 (Dust Control)	Scenario #2 (More Frequent Dust Control)
Directional						
1	0.308	-1.071	0.011	0.479	0.002	0.003
2	0.417	-1.856	0.022	0.992	0.004	0.005
3	0.852	-4.881	0.048	2.729	0.007	0.009
4	1.774	-16.475	0.125	9.098	0.016	0.021
Area-wide Average	1.252	-8.237	0.078	4.963	0.008	0.011

For the directional receptor having the highest impact, the building evacuation control scenario has a cost ranging from \$0.231 million per μg/m³ TSP air quality improvement to \$3.639 million. The control for PM10 costs about two times as much as TSP control. The area-wide average cost for TSP control is \$2.184 million per μg/m³.

Vehicular Traffic

The cost per μg/m³ for controlling fugitive emissions from unpaved roads and parking lots by dust suppression (once every other month) and twice weekly vacuum sweeping of paved roads ranging from \$0.002 million to 0.012 million for TSP. Controlling PM10 is slightly more expensive. The area air quality improvement has a cost of \$0.006 million per μg/m³. The more frequently road cleaning program has a cost/benefit slightly higher than the first scenario.

CONCLUSIONS

Cost/benefit analyses of RACT (Scenario #1) and a more stringent control strategy (Scenario #2) reveal that control of non-traditional fugitive emissions from roads and parking lots are most cost effective. When considering TSP area-wide air quality impacts, RACT control of emissions generated by vehicular traffic is seven times more cost effective than RACT control of blast furnaces and 190 times more effective than RACT control of BOF operations. Road controls are also most cost effective when considering the receptors of highest impact, but the different between that RACT control program and RACT controls of blast furnaces and BOF are reduced to a factor of 2.5 and 140, respectively. The same general relationship between RACT control programs is found when PM10 air quality impacts are considered.

Of the more stringent controls program, road controls are much more cost effective than blast furnace and BOF controls. Area-wide TSP and PM10 air quality impacts show road controls to be 270 and 450 times more effective, respectively, than blast furnace controls. More stringent controls of BOF emissions result in a degradation of air quality when compared to RACT and uncontrolled emissions.

This analysis was done for a "typical" plant. Specific iron and steel mills have unique characteristics and the cost/benefit relationship may change, but the analysis procedure described in this paper is an effective tool to aid decision making.

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AIR QUALITY AND EXPENDITURE EFFECTIVENESS BENEFITS FOR VARIOUS AIR EMISSION CONTROL SYSTEMS AT U. S. STEEL CORPORATION

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ABSTRACT

In the 1970s the domestic steel industry, including U. S. Steel, spent billions of dollars for air emission hardware controls, implemented innovative operating techniques that minimized air emissions, initiated control of non-traditional sources, implemented improved process controls, and worked with the agencies in improving quality control of particulate matter sampling devices. These factors resulted in significant reductions in monitored air quality readings near iron and steelmaking facilities. (Currently all major agency sampling devices in close proximity to the U. S. Steel plants show attainment with the primary annual ambient air quality standard.) This paper discusses the influence of the above factors with respect to measured and projected air quality improvements. The paper provides information on expenditure-effectiveness for various iron and steelmaking controls. The information indicates that controls of nontraditional sources such as road dust are relatively expenditure-effective. Partial building evacuation and baghouse control of secondary BOP shop emissions such as installed at the Edgar Thomson Plant in Western Pennsylvania is about 300 times more expensive than road dust control on the basis of pound per hour of emission reduction and about 700 times more expensive on a projected microgram per cubic meter of suspended particulate air quality.

INTRODUCTION

In the 1970s the steel industry, including U. S. Steel Corporation, spent billions of dollars for air emission controls. A review was made of air quality monitor readings near U. S. Steel facilities over the last decade to attempt to define trends and benefits associated with these large expenditures.

The air quality data was obtained from various published reports by the government agencies. Annual data was reviewed to establish trends. The data conclude that substantial reductions have occurred since the early 1970s and continue into the 1980s.

Expenditures for controls, lower production levels, innovative process technology, control of nontraditional sources such as road dust, and improved quality control of monitoring devices have all played important roles in lowering measured particulate matter air quality levels.

Various coke-oven, and iron- and steelmaking controls were evaluated on the basis of expenditure effectiveness. Dollars of authorized capital per pound per hour of emission reduction and dollars of authorized capital per microgram per cubic meter of air quality improvement were estimated and tabulated. This evaluation showed that road dust controls, coke oven charging, and innovative suppression technology controls were relatively expenditure-effective. BOP secondary baghouse control was not very expenditure-effective as compared to road dust control.

AIR QUALITY PROGRESS

Recently a progress report by the Business Round Table referred to reports by the Council on Environmental Quality, Federal EPA, and the Conservation Foundation and mentioned the improvements in national ambient air quality and level of emissions that have occurred (1)*. All of us as representatives of the environmental agencies, the public, and industry can be proud of these accomplishments. The steel industry in particular has spent 5.6 billion dollars during the past 30 years for air and water quality control facilities and has played a key role in minimizing air emissions and improving community air quality (2).

Using U. S. Steel Corporation (USSC) facilities with which, of course, I am most familiar, please note the suspended particulate matter improvements made over the last several years near our major steelmaking facilities (see Table I). The data have been obtained from various agency sampling reports. Annual geometric mean values are shown. Data below 75 $\mu g/m^3$ are in attainment with the primary ambient air quality standard. In western Pennsylvania suspended particulate matter air quality improved from 153 to 54 $\mu g/m^3$ near the Edgar Thomson plant at the North Braddock sampling station over the period 1973 to June 1983; near Homestead Works the Swissvale Station improved from 155 to 58 $\mu g/m^3$; near the Clairton Coke Works, air quality improved at the Clairton Station from 120 to 44 $\mu g/m^3$ and at the Liberty Borough Station from 112 to 44 $\mu g/m^3$; and near Duquesne Works, air quality improved at the Duquesne No. 1 station from 116 to 51 $\mu g/m^3$. In fact, all 37 monitoring stations in Allegheny County, Pa., now show attainment and, as you know, Allegheny County including Pittsburgh is a large industrial area with several other steel firms

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* See References.

TABLE I. PARTICULATE MATTER AIR QUALITY MONITORS NEAR U. S. STEEL PLANTS
Annual Geometric Mean - Micrograms per Cubic Meter

Plant	Station	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
E-T (PA)	N. Braddock	153	141	115	104	118	110	97	77	74	56	54 (6/83)
Homestead (PA)	Swissvale	-	-	155	118	127	136	108	81	79	62	58 (6/83)
Clairton (PA)	Clairton	120	108	109	90	99	94	78	86	53	45	44 (6/83)
Clairton (PA)	Liberty Boro	112	115	107	96	91	76	77	78	68	46	44 (6/83)
Duquesne (PA)	Duquesne #1	116	118	107	100	108	106	96	79	69	55	51 (6/83)
Fairless (PA)	Bristol							57	53	51	48	
Fairless (PA)	Bordentown							51	45	40	43	
Gary (IN)	Federal Bldg.	111	122	84	106	99	110	111	105	106	76	65 (6/83)
Fairfield (AL)	Fairfield	124	89	74	77	75	77	68	74	73	49	45 (6/83)
Lorain (OH)	Lorain Prod.		74	83	62	77	74	110	71	65	59	
Lorain (OH)	42nd Street		65	66	49	64	57	69	54	52	42	
Geneva (UT)	Provo	82	88	75	95	82	75	79	70	-	-	
Geneva (UT)	Linden	70	77	67	116	84	74	83	74	64	47	
South (IL)	Water Filtration	68	68	67	67	78	61	73	73	66	51	45 (6/83)

besides U. S. Steel Corporation. At Fairless Works near Philadelphia, air quality has been in attainment over the last several years at levels of about 45 $\mu g/m^3$. At Gary, Indiana, air quality improved from 111 in 1973 to 65 $\mu g/m^3$ by mid-1983. Fairfield, Alabama has improved from 124 to 45 $\mu g/m^3$ by mid-1983. At Lorain, Ohio, air quality at the Lorain Products Station improved from a high of 110 to 59 $\mu g/m^3$ and from a high of 69 to 42 $\mu g/m^3$ at another Lorain station. At Geneva Works (Utah), air quality has improved from a high of 116 $\mu g/m^3$ in 1976 to 47 $\mu g/m^3$ at the Linden Station by end of 1982. Near South Works (Chicago, Illinois) at the water filtration station, air quality levels improved from 68 in 1973 to 45 $\mu g/m^3$ by mid-1983.

The above information shows that at the present time all of the above sampling facilities near U. S. Steel's major coke, iron- and steelmaking facilities are in compliance with the primary annual ambient air quality standard.

Some of you may question the reasons for the improvements. Some recent newspaper articles and publications hint that the air quality improvement is due solely to reduced operations (3). The Illinois Division of Air Pollution Control in their June 1983 Air Issues report indicated that there was a tremendous drop in particulate levels in 1982 and that although the agency has not quantified the reasons for the reductions, the agency believes that the influential factors for the reductions are:

1. Emission reductions due to pollution control programs being implemented in 1982;
2. Recession-related production cutbacks;
3. Above normal precipitation at the end of the year;
4. The installation of passive loading restrictors to prevent erroneous measurement due to wind-blown particles adhereing to the filters on days when the hi-vol sampling device is not running (4).

From observing air quality levels near U. S. Steel facilities for the last decade, I believe that all of the above-mentioned Illinois factors are significant. I would like to further comment on Illinois' reasons for the air quality improvement with respect to steel-related sources and add several other technology items that are contributing factors to improved air quality levels near steel facilities in the 1970s and 1980s.

EMISSION REDUCTIONS DUE TO POLLUTION CONTROL

The steel industry has spent several billion dollars for air emission controls (2). U. S. Steel alone has authorized about $1 billion for air emission controls since 1950. These authorizations include some of the most basic controls (cyclones) to some of the most sophisticated and expensive;

i.e., building evacuation and baghouse control of electric furnace shop, coke oven gas desulfurization, and coke oven quench water biological controls. There is no question that the overall expenditure of these tremendous amounts were a factor in air quality improvement even though some of the installed facilities were not cost effective.

RECESSION-RELATED PRODUCTION CUTBACKS

The steel industry has had a significant decline in production in 1982 and 1983 (2). In 1982 U. S. Steel's production was at the lowest level since 1938. In 1983, raw steel production levels are running about 45-60 percent of capability, although some facilities such as Gary Works, Indiana are operating at relatively higher levels in 1983 than a year ago.

For those who believe that production level is the sole factor for improved air quality levels, the following is highlighted.

1. In 1981 U. S. Steel's production levels at Edgar Thomson, Duquesne, Gary, Lorain and Geneva were almost identical to the levels of 1975. In fact, rather than a decrease, there was a slight increase (3%) overall for these plants in 1981 when compared to 1975 levels. Of the six stations in Table I that monitor air quality near these plants in 1975 two of the six stations were attainment and the overall mean for the six stations was 87 $\mu g/m^3$. In 1981 five of the same six stations near U. S. Steel facilities in Table I were in attainment with primary annual standards when production levels were slightly higher (3%) and the overall mean for the six stations was calculated at 61 $\mu g/m^3$ or 30 percent lower than in 1975. With adjustments for background levels percentage reductions would even be substantially greater than 30 percent.
2. Production levels at the Gary plant have been 9 percent higher for the period 7-1-82 to 6-83 than the period 1-1-82 to 12-31-82, yet air quality levels have dropped an additional 11 $\mu g/m^3$ from 76 to 65 $\mu g/m^3$ during the 82-83 period.

ABOVE NORMAL PRECIPITATION AT END OF YEAR

Above normal precipitation would be a factor in minimizing nontraditional sources such as road dust and storage piles, open lots, etc. A number of studies have shown these non-point sources do contribute significantly to air quality. A 1979 study near steelmaking facilities in Allegheny County, Pennsylvania, at selected sampling sites indicated that, after background levels were subtracted, nontraditional sources such as road dust and storage piles contributed 78.8 percent of particulate loading (5). This subject will be discussed later in more detail.

INSTALLATION OF PASSIVE LOADING RESTRICTORS

The installation of passive loading restrictors (sample savers) in the late 1970s and early 80s, has had a tremendous effect on air quality monitor readings by increasing the sampling accuracy. The passive loading restrictor is a quality control device for the sampling monitors. It minimizes the effects of windblown emissions which previously adhered to the sample filter on days when monitor was not being operated. For example, filters are commonly placed in the field but sampling is not initiated until six days thereafter. Allegheny County (Penna.) has been very involved with monitoring the differences associated with improved quality control via use of sample savers. Data from two Allegheny County monitors, one with and the other without a sample saver, located at the same site over many months (8-7-79 to 4-27-80) showed reductions of 6 $\mu g/m^3$ at the Liberty Station (near Clairton Coke Works). A similar study showed a difference of 16 $\mu g/m^3$ at Avalon Station (near coke plant, blast furnace, cement plant, heavy traffic area) (6). Interestingly, it should be kept in mind that these side-by-side monitors are affected by the same production, control and emission levels, and meteorology and precipitation levels. For the year 1980 the installation of a sample saver was the difference between attainment (71 $\mu g/m^3$) and nonattainment (78 $\mu g/m^3$) values at the Liberty Borough Station near Clairton Coke Works as indicated by two side-by-side monitors at same location.

Based on data in the Mon Valley, Pennsylvania, and Gary, Indiana, sample savers are very significant. Many agencies have recognized this increased accuracy and are now utilizing sample savers at monitoring stations. All agencies should be using them unless filters are installed and replaced daily.

IMPLEMENTATION OF ROAD DUST AND STORAGE PILE NONTRADITIONAL SOURCE CONTROLS

With respect to road dust and storage pile nontraditional sources, we are very cognizant of the significant effect of these sources on air quality levels. In 1977 we were dismayed that air quality levels at the Glassport Station near Clairton Coke Works increased by 50 $\mu g/m^3$ even though we authorized expenditures over $95 million for air emission controls at Clairton. Subsequent checking indicated that the increase was due to a new source of road dust from heavy traffic near the monitor.

For year 1982 all stations in Allegheny County, Pa. showed attainment with the primary standard with the exception of a station that was heavily influenced by road dust. At the request of the county agency, U. S. Steel agreed to utilize wet suppression materials on this road which was located about one mile from our plant. The latest sampling results show that road dust must be a significant contributor since that station has dropped from a high of 112 $\mu g/m^3$ (October, 1980 to November, 1981) to 57 $\mu g/m^3$ (April, 1982 to March, 1983) after implementation of a road dust suppression program. Of course, these two examples are not uncommon. In 1979, consultants hired by Allegheny County and by the steel industry demonstrated that, based on extensive modeling and community sampling, and after making adjustments for background, the industrial point source contribution to key monitoring sites was estimated to be only 11.1 percent, other traditional sources were estimated at 10.0 percent, but nontraditional source such as road dust and storage piles contributed 78.9 percent, the highest amount (5).

Shenango, Inc., has also implemented a road dust control program in Allegheny County. This program by Shenango was approved by the agencies and has resulted in Shenango not installing expensive blast furnace casthouse controls (7). Many months after approval of the road dust program, air quality levels have improved at the Avalon Station and were 57 $\mu g/m^3$ during the period 6-82 to 5-83.

Armco, Inc., at Middletown, Ohio, has also developed a bubble program based on nontraditional road and storage pile controls. After installation of the road dust-storage pile program and with high production, particulate levels have dropped substantially and ambient levels below the primary standard have been attained at all stations. Specifically before control (August 1979-July 1980) nine sampling stations averaged 77 $\mu g/m^3$ and production was 160,780 tons per month. After control (August 1980-July 1982) the same nine sampling stations averaged 62 $\mu g/m^3$ although production increased by 27 percent to 204,134 tons per month. Baghouse controls were not installed on the iron- and steelmaking secondary sources such as the blast furnace casthouse and the BOP and open hearth shop (8).

At the present time, all of U. S. Steel plants have implemented some type of road dust control program. The intensity of the programs has been increased the last several years when substantial drops in particulate levels have been observed.

IMPLEMENTATION OF IMPROVED STEEL PROCESS CONTROL TECHNOLOGY IN 1970-1980s

Steel production requires complex physical and chemical transformations induced by intense heat and pressure. Therefore, continuous development and application of sophisticated technical skills, production equipment and process controls are necessary. Computer control, for example, has been an integral part of steel production efforts in the 1970s and 1980s. They are important in improving productivity and monitoring actual production operations at the coke ovens, blast furnace, steelmaking furnaces, continuous casting, and finishing facilities.

U. S. Steel Corporation has made substantial progress in coke oven, blast furnace and steelmaking operations in the 1970s-1980s. Older coke ovens and blast furnaces have been modified to improve productivity. A continuous caster at Gary has been completely revamped and a new caster has been built at Lorain which will improve productivity and reduce energy requirements. There have been substantial air quality improvements associated with the improved steel process control technology. For example, at Fairfield, Alabama, USSC installed a new blast furnace, coke battery and BOP shop to replace older facilities. If air emission controls had been installed to meet the SIP requirements on the previously operated steelmaking facilities—rather than modernization—approximately 700 more tons per month would have been emitted. The effectiveness of the new blast furnace, coke and steelmaking modernization facilities on air quality levels is demonstrated not only by reductions of about 3,000 tons per month of emissions at the Fairfield plant but, most importantly, by improvements in community particulate levels from the high values of 124 $\mu g/m^3$ in 1973 to 74 $\mu g/m^3$ in 1974 shortly after completion of the facility program.

Blast furnace developments also exemplify the technological progress being made. In 1971, the domestic steel industry required 219 blast furnaces to produce 81.7 million tons of iron. Ten years later, it required only 129 blast furnaces to make 73.6 million tons of iron. Improvements in the quality of charged raw materials and process control advances were important factors in the gain in efficiency and the minimizing of potential emissions (2). For example, coke rates have been significantly reduced at blast furnaces in the 1970s-80s. Utilizing less coke at the blast furnaces mean lower coke production requirements at the coke plant. We have calculated that improving the coke rate at a blast furnace from about 1430 to 1060 lb to produce a ton of iron could eliminate—back in the process at the coke plant—700 lbs/day of controlled particulate from being discharged into the atmosphere from charging, door, pushing, quenching, stack, and material handling operations. In addition to the particulates saved by the improved coke rate, potential emissions of 1180 lbs/day of sulfur oxide could be avoided. In addition to the potential air emission savings, controlled waste water discharges of 130 lbs/day of total suspended solids, 11 lbs/day of oil, 16 lbs/day of NH_3-N and 4 lbs/day of organics would be avoided. Finally, the calculations indicate that a potential of 1180 lbs/day of solid waste for disposal would be avoided.

In a similar manner, it has been calculated that a new caster which increases yield and thereby reduces requirements for coke, iron, and steel could improve potential controlled environmental emissions by 880 lbs/day of particulates, 1070 lbs/day of sulfur oxides, 220 lbs/day of total suspended solids, 10 lbs/day of oil, 20 lbs/day of NH_3-N, 4 lbs/day of organics, 1 lb/day of metals and reduce potential solid waste disposal of 571,000 lbs/day, most of which is blast furnace slag. The above does not include the potential reduction of coal used to generate the electricity which translate into emission reduction of 250 lbs/day of particulates, 24,000 lbs/day of solid wastes, and 2060 lbs/day of sulfur oxides which are becoming of greater concern today with possible formation of acid rain.

Continuous casters have been built by the domestic steel industry in the 1970s and are continuing into the 1980s. At the end of 1982, 29 percent of this country's raw steel was continuously cast. Between the beginning of 1982 and the end of 1984, domestic steelmakers will have installed 16 new continuous casters with an annual capacity of 16 million net tons (2). It is important that in examining alternatives for obtaining further environmental improvements that productivity gains be included.

DEVELOPMENT OF INNOVATIVE AIR EMISSION CONTROL TECHNOLOGY WITH EMPHASIS ON CONTROL AT THE SOURCE

In the early 1970s, the most important source of steel-related air emissions resulted from coke oven operations. The solution to several of the major sources of coke plant air emissions—charging, doors and top-side emissions—did not result from major capital investments but resulted from development of innovative and sophisticated operating and maintenance techniques which emphasized prevention of emissions at the source. For example, at U. S. Steel Corporation, charging and door emissions were difficult technical problems that were ultimately solved by special task force groups consisting of operators, engineers, and researchers who perfected control systems to meet the technology-forcing standards of the Clean Air Act. Advanced operating technology for stage charging, and door sealing was developed by U. S. Steel. (I might add some of the above technology was shared with the industry at a meeting two weeks ago in Pittsburgh.) At Clairton, these techniques resulted in significant reduction in emissions. Charging emissions were improved from an average of about 50 seconds per charge to about 10 seconds per charge in the late 1970s and door emissions, from a plant average of about 45 percent leakage to about 5 percent over the period 1974 to 1980. The improved emission levels possibly contributed to improved air quality in the region. In 1973, there were 11 air alerts in Allegheny County, Pennsylvania; in 1977, six alerts; and for the last three and one-half years, there have been no air pollution alerts in the area (9).

In addition to coke plant control technology, U. S. Steel and others have developed suppression techniques which have been very effective in reducing emissions from iron and steelmaking sources. J&L has developed a proprietary process for emission reduction during ironmaking (10). U. S. Steel has released to the industry and government technology for minimizing iron- and steelmaking emissions with suppression technology which minimizes air emissions at the source. These techniques not only offer appropriate emission control but also provide improvements to the workplace environment.

EXPENDITURE-EFFECTIVENESS OF VARIOUS CONTROL SYSTEMS

As previously mentioned, U. S. Steel Corporation has authorized about one billion dollars for air emission controls. U. S. Steel has installed almost every type of air emission control device and has developed innovative and sophisticated process technology and improvements at the source. In many cases, installation of these controls have resulted in improved community air quality values. In other cases air quality improvements have not been readily discernible. In some cases, the improvements in air quality were very expensive and in other cases, the expenditure-effectiveness ratios (authorized capital per pound per hour of controlled particulate matter) were very favorable. The following provides information in an attempt to categorize emission control methods with respect to expenditure-effectiveness for various steelmaking sources.

From an expenditure-effectiveness standpoint, the operating improvements and techniques which significantly reduce charging emissions (stage charging) were extremely positive. For example, at Clairton, authorizations of about 3 million dollars* were made for additional steam aspiration and larry car modifications. Estimated benefits from improved charging performance was a reduction of about 860 lbs per hour of emissions at Clairton.

USSC also authorized about $71 million to control pushing emissions at Clairton by the installation of hardware controls. These controls had a relatively high-expenditure/low-effectiveness ratio since estimated emission reduction of about 320 lbs/hr resulted.

An electrostatic precipitator which projects to a 1983 cost of $6.4 million was installed on the No. 21 combustion stack at Clairton; little air quality improvement has been indentified with this installation. In fact, USSC researchers, engineers, and operators subsequently developed improved operating techniques for the control of stack emissions and no additional precipitator controls have been installed at any U. S. Steel battery stack. Coke quenching emissions supposedly were the largest single source of particulate matter in Allegheny County. As a result, quenching controls were authorized and installed at a cost of about $61.2 million. Suspended particulate matter air quality levels did not show improved values commensurate with the installation of quench controls and the anticipated reductions.

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* For comparison purposes, all dollars in report have been updated to 1983 dollars using a U. S. Steel inflationary index. In some cases 1983 technology could have resulted in a significant lower expenditure as compared to control systems installed in mid-1970s.

In the early 1970s a source of great concern to the agencies was steel scarfing emissions. Estimates of 20 pounds of emissions for every ton of steel scarfed were published (11). Because of these published estimates expenditures for controls of several million dollars were mandated at several facilities. Once the controls were installed, tests conducted showed that the emissions ducted to the control device were less than one percent of those estimated. Expenditure-effectiveness for the scarfing device is relatively high. At Lorain Works, a $2.2 million scarfer resulted in an emission reduction of only 22 lbs/hr. Undoubtedly the visible emission plume of the scarfer led engineers to estimate emissions one hundred times higher than actual.

Several other steelmaking process emission sources have intermittent visible emission plumes emitted from high exit points which are readily discernible.

USSC recently installed a $12.2 million BOP secondary control device at Edgar Thomson Works in western Pennsylvania. After completion of the installation, including sealing off a large portion of the roof, tests indicated fugitive emission captured to be 43 lb/hr (12). Expenditure-effectiveness index for this control has been calculated at $285,000 per pound per hour of particulate emissions.

Probably the source receiving the most attention today is the blast furnace casthouse. A consultant for USSC has measured the emissions leaving a Fairless blast furnace casthouse monitor and has obtained relatively low values, approximately 0.1 lb/ton (13). USSC has installed at Edgar Thomson Works a local hood system over the trough area which draws emissions and via an air curtain pushes emissions at high velocities into a local hood. Emissions forced into the local hood system have been measured at about 0.2 lb/ton (14). At another casthouse, emissions have been measured over the slag and iron runners at about 0.15 lb/tons (15). The sum of the trough and slag and iron runners would be about 0.35 lb/ton. Of course, these emissions may vary from casthouse to casthouse. Other companies and agencies have reported emissions in the range of approximately 0.1 to 0.78 lb/ton (16). The expenditures required to install controls on these casthouse facilities can range from about $200,000 to as high as $15.1 million. The $200,000 is the estimated expenditure for USSC suppression technology; the $15.1 million expenditure figure is for a local hood system over the trough and runners, evacuated to a baghouse at a large blast furnace casthouse. Assuming $15.1 million would be spent to capture emissions of 0.4 lb/ton, the emissions expenditure-effectiveness index is about $105,000 per lb/hr. For innovative suppression technology and along with advanced operating and maintenance practices it is estimated that reductions of about 110 lbs/hr can be obtained by spending approximately $200,000 or $1800 per lb/hr. The basis for this suppression system was developed by USSC researchers, engineers, and operators. The agencies have been informed and have been very helpful in supporting the developing technology. USSC has also agreed to share the technology with the agencies and industry.

With respect to road dust and storage pile nontraditional sources, we estimate that at road dust sources at Duquesne Works, we can minimize road dust emissions by about 320 pounds per hour by spending about $200,000 capital for mobile suppression equipment.

To summarize, an expenditure-effectiveness index of various steelmaking sources has been compiled. Authorized expenditures over the years have been escalated to 1983 dollars using inflationary factors for comparison purposes. Wherever possible, actual test results by USSC were utilized to define emission rates (12,17). Where test results were not available, emission factors and engineering judgment were used (16). Table II ranks the sources and indicates that road dust and blast furnace suppression controls and coke oven charging controls are relatively expenditure-effective whereas BOP secondary baghouse controls, coke pushing and quenching are several orders of magnitude higher with respect to potential environmental benefit.

TABLE II. EXPENDITURE EFFECTIVENESS FOR VARIOUS STEEL PLANT CONTROL SYSTEMS (1000 DOLLARS PER POUND PER HOUR OF AIR EMISSION REDUCTION)

Road Dust Controls	1
B.F. Casthouse Suppression	2
Coke Charging	4
B.F. Casthouse Baghouse	100
Scarfer Wet Precipitator	100
Coke Combustion Precipitator	130
Coke Quenching-Biological Treatment	180
Coke Pushing Scrubber Car	220
BOP Secondary Baghouse	290

In addition, modeling of the air quality effects was conducted for the various sources mentioned in Table II. Lorain Works stack parameters and the ISC (Industrial Source Complex Model) were utilized in the calculations. Calculation for expenditure-effectiveness in terms of dollars per microgram at maximum impact of air quality have been made and the results are illustrated in Table III.

Again, road dust controls, coke charging and blast furnace suppression technology are relatively cost-effective with respect to modeled air quality

TABLE III. EXPENDITURE EFFECTIVENESS FOR VARIOUS STEEL PLANT CONTROL SYSTEMS (10,000 DOLLARS PER μg/m^3 OF AIR QUALITY IMPROVEMENT)

Road Dust Controls	1
Coke Charging	3
B.F. Casthouse Suppression	8
Scarfer Wet Precipitator	17
Coke Pushing Scrubber Car	200
B.F. Casthouse Baghouse	410
BOP Secondary Baghouse	670
Coke Quenching-Biological Treatment	1030
Coke Combustion Precipitator	1250

benefits and coke combustion precipitator controls, coke quenching biological controls and BOP secondary baghouse controls are much more expensive.

A review of the data near our plants also indicates that installation of BOP secondary baghouse controls and blast furnace casthouse baghouse controls did not appear to be a key factor in actual air quality levels improving from nonattainment to attainment. For example, at Edgar Thomson Works (in Pennsylvania), the North Braddock Station went from 153 μg/m^3 suspended particulate matter in 1973 to 74 μg/m^3 in 1981. The BOP secondary baghouse controls ($12.2 million) were not completed until November 1982. There were no casthouse baghouse controls at Edgar Thomson when the North Braddock air quality station improved from 153 μg/m^3 to 77 μg/m^3 in 1980. Blast furnace local hood controls with a baghouse were added on one furnace in mid-1981 along with partial road dust controls and air quality improved from 77 μg/m^3 to 74 μg/m^3.

At the Duquesne plant, air quality suspended particulate matter levels improved from 116 μg/m^3 in 1973 to 79 μg/m^3 in 1980 and to 69 μg/m^3 in 1981. At Duquesne, no secondary baghouse controls have been added and suppression controls at No. 6 blast furnace casthouse were added in late 1982. Interestingly, blast furnace production was higher in 1981 than 1980 at Duquesne and if blast furnace emissions were a significant factor, levels should have been higher in 1981 but were 10 μg/m^3 lower than in 1980. Partial road dust controls in 1981 may have played a larger part in improving air quality.

At Gary, Indiana, air quality suspended particulate matter was 106 μg/m^3 in 1981, 76 μg/m^3 in 1982, and 65 μg/m^3 in 1983. No BOP or casthouse baghouse controls were installed during 1982 when levels dropped from 106 to 76 μg/m^3. Production did decrease in 1982 but has increased in 1983 when levels are

11 $\mu g/m^3$ lower. Improved partial road dust controls in 1982 and 1983, improved quality control of sampling including sample savers, partial suppression technology on blast furnaces, and improved process technology at blast furnaces and coke ovens may have been primarily responsible for air quality levels dropping to 65 $\mu g/m^3$ over the period 7-82 to 6-83.

At Fairfield, Alabama, the new BOP shop, coke battery and blast furnace coincided with a drop in air quality suspended particulate matter levels from 124 $\mu g/m^3$ in 1973 to 74 $\mu g/m^3$ in 1975. From 1975 to 1981, air quality remained relatively constant, i.e., 74 $\mu g/m^3$ in 1975 and 73 $\mu g/m^3$ in 1981. During the 1975 to 1981 period, secondary baghouse controls at the mixer and at one BOP vessel were added at the BOP shop but no appreciable change in air quality level was noted. At the remaining plants—Fairless, Geneva, Lorain, and South—levels have shown attainment for a number of years. Attainment at the plants cannot be attributed to installation of secondary steelmaking baghouse controls or to the installation of baghouse controls at the blast furnace casthouses.

SUMMARY

As previously mentioned, all of us can be proud of air quality accomplishments that have been attained in the mid-1970s and early 1980s. We in industry probably have achieved performance and accomplishments that we did not think were possible via the technology-forcing concept of the Clean Air Act. I personally, for example, in the early 1970s did not believe coke oven doors could attain a 5 percent visible emission standard on a day-in/day-out production basis. But our operators, researchers, and engineers subsequently were able to develop techniques that proved that proper design and operating and maintenance practices can be extremely effective. Our expenditure data shows that innovative suppression technology installed on iron- and steelmaking sources is very favorable with respect to the potential air quality benefits. In later years the environmental agencies have played a key role in providing support and encouragement of alternative expenditure-effective controls.

We installed a number of controls that had high expenditure, low benefit performance. Some sources such as road dust were not stressed in a timely manner which undoubtedly resulted in higher expenditures for secondary iron- and steelmaking controls which were thought to be necessary to attain primary standards. The significance and importance of improved productivity, product yields, and lower energy requirements associated with the modernization of blast furnaces and installation of casters and BOP shops were not generally recognized.

Over the next several years, if we are to maintain the air quality standards in the most effective manner, it is our belief that emphasis should continue to be on conscientious operation and self-monitoring of existing steelmaking air controls, utilization of suppression technology, and there should be additional emphasis on control of road dust and storage piles. Additional installations for high expenditure, low benefit secondary baghouse controls at iron- and steelmaking facilities should not be imposed unless further reductions are clearly necessary to maintain primary ambient air standards. In addition, environmental incentive, not disincentive, should be given for installation of modernized steelmaking facilities that improve productivity, energy usage, and yield such as continuous casters and facilities for better blast furnace productivity, which in turn improve coking rates and substantially reduce potential air emissions.

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VALIDATION OF ISC IN COMPLEX TERRAIN AND USE IN ATTAINMENT REDESIGNATION

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ABSTRACT

This paper discusses how the Industrial Source Complex (ISC) model and model options were approved for use in complex terrain and how an area that was in non-attainment for TSP was reclassified to attainment with the aid of a validated ISC model. This effort was completed as part of the cast-house emissions trade study conducted for Shenango, Incorporated at its Neville Island facility.

As a general policy for complex terrain, no air quality model is available to adequately serve as a tool in making an attainment demonstration for industrial type sources. The problem was solved by modifying the ISC model with agency approval to serve as a tool in developing an attainment redesignation case.

The use of model options, meteorological data, emissions inventory data and receptor locations led to a validated ISC model in complex terrain. An independent test using receptor-modeling yielded a favorable correlation to the validated ISC results. After validation of the model, this paper discusses how a determination was made of the future attainment status of the area near the Neville Island facility.

This approved validation technique can be used by most sources in complex terrain either for emissions trades already in attainment or for developing a redesignation program for attainment before developing an emissions trade.

INTRODUCTION

For a source that is in a non-attainment area that lacks the necessary quarters of ambient air quality data to be reclassified into attainment, an air quality dispersion model can be used to show the area can be reclassified or develop a control strategy to bring the area into attainment. In order to utilize the model for attainment demonstration, the model must be validated.

This paper discusses the validation of the Industrial Source Complex (ISC) model and its use in the attainment demonstration. These two processes were used as part of the Shenango Alternative Emission Reduction Option[1] (AERO) for Total Suspended Particulates (TSP) at their Allegheny County, Pennsylvania facility. Much of what is presented below is the result of the efforts with several agencies. An Agency Coordinating Committee consisting of representatives from the Bureau of Air Pollution Control of Allegheny County, the Pennsylvania Department of Environmental Resources and the U.S. Environmental Protection Agency provided input to many of the issues described below through technical subcommittees. This paper presents those elements of the study related to the attainment redesignation through air quality modeling.

DEVELOPMENT OF A VALIDATED MODEL

There are four basic elements required before air quality modeling can be undertaken for any year:

- Selection of model and model options;
- Preparation of the meteorological data;
- Preparation of the emissions inventory; and
- Selection of receptors.

The four elements, along with the validation of the ISC model, are described below.

ELEMENTS OF MODELING

The Environmental Protection Agency (EPA) states that specific input selection for these elements and ultimate use of the model is to be solved on a case-by-case basis. Thus, the overall process by which one selects a model and input data is described below. An iterative process was used with the Agency Coordinating Committee to resolve the technical issues that are presented below. The specific values are not presented in this paper because they depend upon many factors outside the intent of this paper.

Selection of Model and Model Options

Shenango is located in the Ohio River basin. The area surrounding the plant has a typical river-valley terrain. No EPA approved model exists, except for the Valley model, which can be utilized in complex terrain. The Valley model was not used because the EPA considers it as a screening model. Many other EPA and non-EPA models were considered. However, only ISC has the capabilities of:

- Simulating line, area, volume and point sources;

- Calculating the effects of gravitational settling and dry deposition;
- Evaluating plume building and stack tip downwash; and
- Separating multiple sources spacially.

Specifically, the long term version of ISC (ISCLT) was chosen because the controlling TSP National Ambient Air Quality Standards (NAAQS) was the annual standard which is 75 μg/m³.

In this attainment demonstration, each of these capabilities is very important in validating the ISC. The EPA, after many discussions, suggested a procedure to modify ISCLT for use in complex terrain. This change allowed for source heights to be higher than the receptor heights. As a result, any plume centerline which was lower than the receptor in height resulted in full impaction. Under this scenario, worst case concentration always occurred. For future reference, this change is called Terrain Impact Mode.

In the development of the emissions inventory, discussed later, approximately 60% of the emissions released were low level. Combining this fact with the complex terrain question, the EPA again, after many meetings with them, suggested a test to determine if complex terrain was important to this attainment demonstration. This test compared the difference between the Terrain Impact Mode and the Flat Terrain Mode (assumes no terrain). Presented in Figure 1 is a schematic cross section by height from the Shenango facility to the highest terrain located in Avalon Township. This figure shows that high elevated sources pass over the top of the hill while low level sources impact the side of the hill. Results assuming terrain were then compared with results assuming no terrain. These differences for any receptor of interest must be less than 10 percent. Results of this test showed a less than 10 percent difference at all receptors. This demonstrated that the low level source impacts dominated. Thus, complex terrain was not considered any further.

The following is a list of other options and features as used in the validation process:[2]

- Inclusion of building and stack tip downwash;
- Inclusion of gravitational settling and dry deposition of particles;
- Use of Urban Mode 2;
- Simulation of roads as a series of volume sources;
- Plume rise as a function of distance; and
- Inclusion of an initial sigma z and y for process and open-dust fugitive sources.

Each of these options provide a more realistic understanding of the dispersion and diffusion characteristics that are necessary for validation of a model.

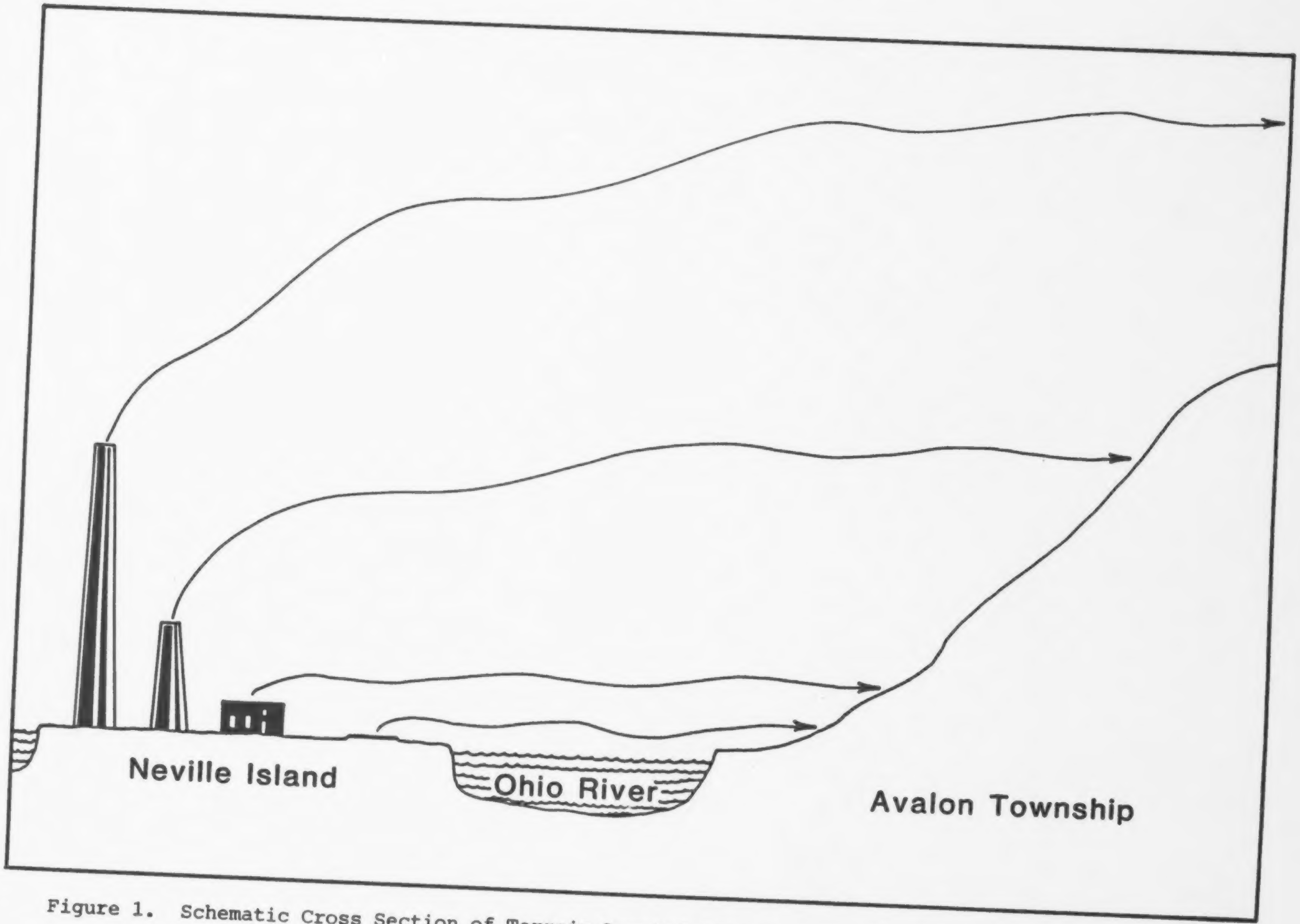

Neville Island
Ohio River
Avalon Township

Figure 1. Schematic Cross Section of Terrain Located Near Shenango Facility Showing Impacts of Sources on Terrain

Preparation of Meteorological Data

River-valley terrain is known to affect wind flow.[3] As described earlier, a river-valley surrounds the Shenango facility. Wind speed and direction data was collected by Shenango for the base year 1979. Greater Pittsburgh International Airport (GPA), located 7 miles to the west of Shenango, supplemented the Shenango plant data to create a joint frequency distribution of wind speed by direction by stability class (STAR). This STAR distribution is directly compatible with ISCLT. Wind rose (STAR without stability) for GPA and Shenango is depicted in Figure 2A and 2B respectively. A classical river-valley flow pattern is shown in Figure 2B. The influence of river-valley meteorology will be discussed later in the paper.

Preparation of Emission Inventory

The three basic types of sources for this plant are process, process fugitive and open-dust fugitive sources. In the development of the emissions inventory, a complete material flow and mass balance was performed.

For the process and process fugitive sources, this was performed by reviewing and analyzing the production data for 1979. For open-dust sources, source testing and a traffic study were performed in 1980.[4] Traffic data was scaled upward to reflect the high production during 1979. All emission factors were reviewed by the EPA prior to the validation of the model.

Additionally, all sources outside of Shenango within the significant impact zone were also included. The significant impact zone is identified as the distance in any direction away from the plant that the annual impact was 1 $\mu g/m^3$. As a result of this analysis, major urban highways and other industrial sources were included in a separate inventory.

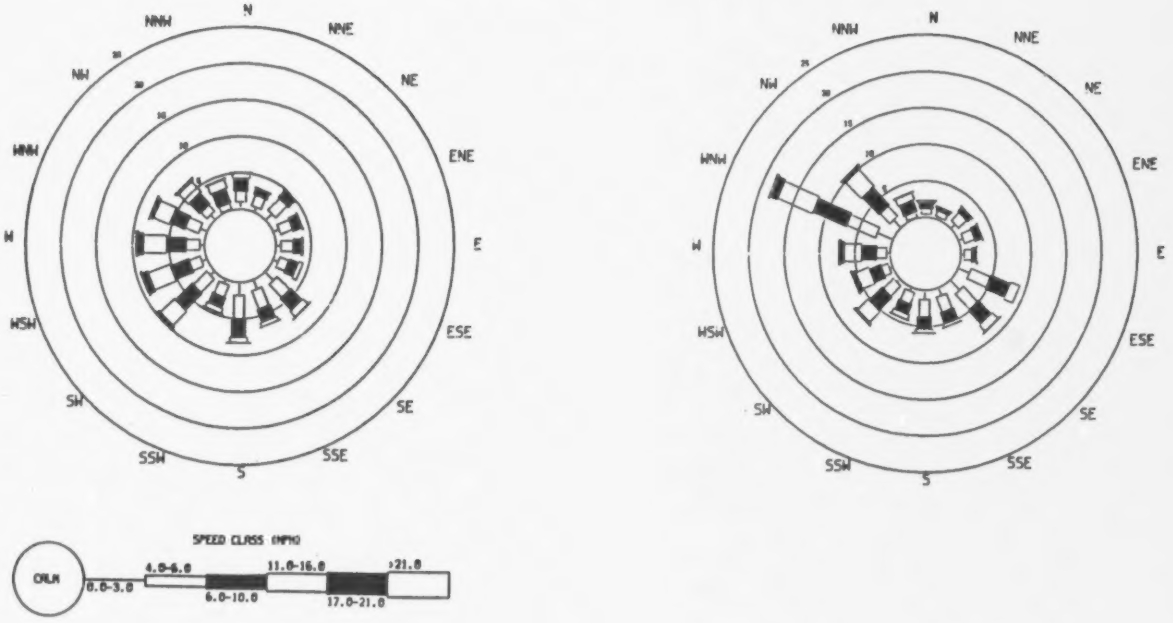
In summary, a total of 108 sources totalling 3513 tons per year were included. This by far was the most comprehensive inventory for that part of Allegheny County.

Selection of Receptors

With the significant impact zone defined, there were only two air quality monitors in the area. These were operated by the Bureau of Air Pollution Control (BAPC) of Allegheny County. These two sites were used in the validation of the model.

VALIDATION OF THE ISC MODEL

After all the elements of modeling have been individually analyzed to provide the most realistic scenario, air quality modeling yields just two of the four components of air quality needed to define the total impact of all sources. The two components that air quality modeling provide are the industrial and urban source components. The other two are the background and residual components. The development and interaction of all 4



(2A)

(2B)

Figure 2. Wind Roses for the Greater Pittsburgh International Airport (2A) and Shenango (2B) for 1979

components of air quality are presented in Figure 3. This figure demonstrates the complexity of modeling.

Background is defined for this demonstration as the component of air quality before it comes into Allegheny County. The residual is defined as the component of air quality that comes from all uninventoried sources in the immediate area and is expected to be a positive number because not all sources of particulate matter in an urban setting can be included in the emissions inventory.

In a separate analysis, the BAPC determined the background to be 48.0 µg/m³. The residual could not be determined until the sum of the three other components of air quality were subtracted from the measured TSP value.

Results of the validation of the ISCLT model are presented in Table 1. Residual for this validation was 7.6 µg/m³. If all the sources in Allegheny County were included in this validation, the residual would be very close to 0 µg/m³.

The sum of the modeling components of air quality and the background component are presented below to demonstrate the overprediction of using the GPA versus Shenango meteorological data in the validation process.

Site	Modeled		Measured
	GPA	Shenango	
Avalon (BAPC-4603)	115.4	94.3	103.1
Bellevue (BAPC-4601)	104.8	88.6	95.0

If one had used the GPA data, the residual would be negative. Because not all sources were inventoried, the residual must be positive. Therefore, the use of more realistic Shenango data, the ISCLT model could be validated. This clearly demonstrates the use of local meteorological data in the validation process.

As an additional check on the validation of the ISCLT model, receptormodeling was used on selected sources. Comparison of the air quality and receptor modeling showed a close comparison. This further showed that the validation was correct.

DEMONSTRATION OF ATTAINMENT

The demonstration process took place in three phases. The first phase was to use the 1979 emissions inventory to determine the status of air quality. The second phase was to use the State Implementation Plan (SIP) mandated emission controls on all sources. Finally, if attainment was not achieved, the third phase was to identify additional emission reductions to bring the area into attainment. Results of each of these phases is described below.

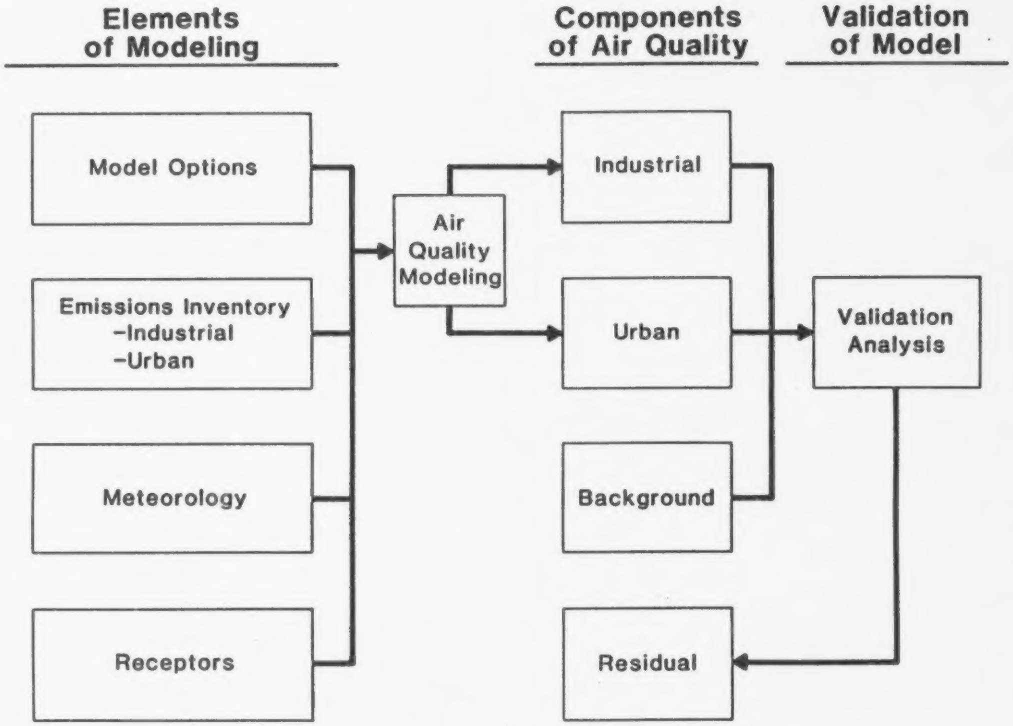

Elements of Modeling
Components of Air Quality
Validation of Model
Model Options
Emissions Inventory
-Industrial
-Urban
Meteorology
Receptors
Air Quality Modeling
Industrial
Urban
Background
Residual
Validation Analysis

Figure 3. Validation Process Used at Shenango Attainment Demonstration

TABLE 1. VALIDATION RESULTS FOR THE AVALON (4603) AND BELLEVUE (4601) BAPC SITES USING EMISSION INVENTORIES, METEOROLOGICAL DATA AND THE ISC MODEL FOR THE BASE YEAR 1979

	Annual Arithmetic TSP Concentration (μg/m³)	
	Avalon	Bellevue
Industrial	29.0	29.7
Urban	17.3	10.9
Background	48.0	48.0
Subtotal	94.3	88.6
Measured	103.1[a]	95.0[b]
Difference	8.8	6.4

Residual = 7.6[c]

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[a] 103.1 = (105 - 10) * 1.086; where 10 is the sample saver and 1.086 is the conversion factor from geometric to arithmetic mean at Avalon (114/105).

[b] 95.0 = (96 - 10) * 1.104; where 10 is the sample saver and 1.104 is the conversion factor from geometric to arithmetic mean at Bellevue (106/96).

[c] 7.6 = (8.8 + 6.4)/2.0.

BASE YEAR EMISSIONS INVENTORY FOR 1979

The purpose for using the 1979 emissions inventory was twofold: 1) to validate the ISCLT model (discussed earlier), and 2) to determine the areawide status of air quality. One hundred (100) receptors were placed spacially to determine the areas of maximum impact otherwise known as hot spots (see Figure 4). If any part of the area was above the TSP annual standard of 75 $\mu g/m^3$, the area would remain in non-attainment. Results of using the emissions inventory for Shenango, major urban highways and other industrial sources in the area and the river-valley meteorological data are graphically shown in Figure 5. In this figure, only the areas greater than 75 $\mu g/m^3$ are shaded. This shows the extent of the non-attainment area.

SIP EMISSIONS INVENTORY FOR 1982

All SIP mandated controls for sources in Allegheny County were planned to be in place by December 31, 1982. These controls are based upon County regulations and Consent Decrees. The purpose for these controls is to bring the area into attainment with the NAAQS.

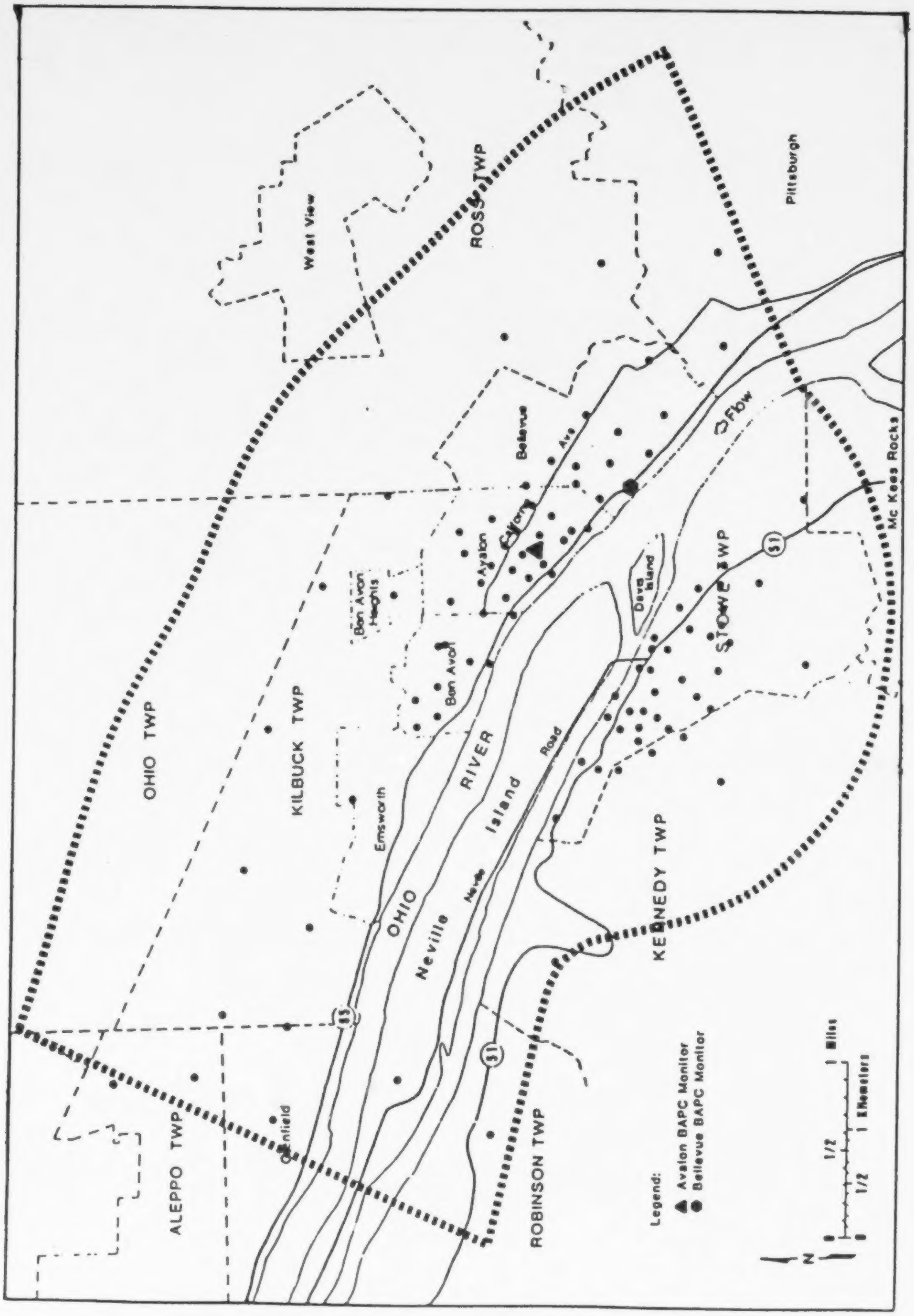
Reasonably Available Control Technology (RACT) for unpaved roads and parking lots in Area 3 of Allegheny County was investigated. Based on a separate analysis, RACT was considered to average 35 percent controls on unpaved roads and parking lots when considering the diversity of control technologies and traffic volumes. Percent controls for other sources were based upon individual SIP requirements and are too numerous to mention in this paper.

The BAPC, in a separate analysis, determined that the background component of air quality would be reduced from 48 $\mu g/m^3$ in 1979 to 45.0 $\mu g/m^3$ in 1982. This was primarily based upon other states implementing their own SIP controls by December 31, 1982. The residual component of air quality as defined earlier must remain the same. The sum of these two components was a constant 52.6 $\mu g/m^3$ for all receptors. This allows a maximum local sources impact that must be less than 22.4 $\mu g/m^3$ for attainment to be achieved.

Results of using the SIP based emission inventory for 1982 are presented in Figure 6. Again, only the areas above 75 $\mu g/m^3$ are shaded. Only one small area just south of Neville Island was above the annual standard for TSP. This small area was strongly influenced from particulate emissions from the two intersecting public highways in the center of the shaded area. Thus the SIP controls on sources in the immediate area did not bring the area into attainment.

ALTERNATIVE EMISSION REDUCTION OPTION EMISSION INVENTORY FOR 1982

A third emission inventory was developed to bring the area into attainment with the NAAQS. This was the AERO emission inventory. This inventory was based upon Shenango applying additional controls beyond SIP on selected sources, while eliminating SIP controls on their blast furnace casthouse.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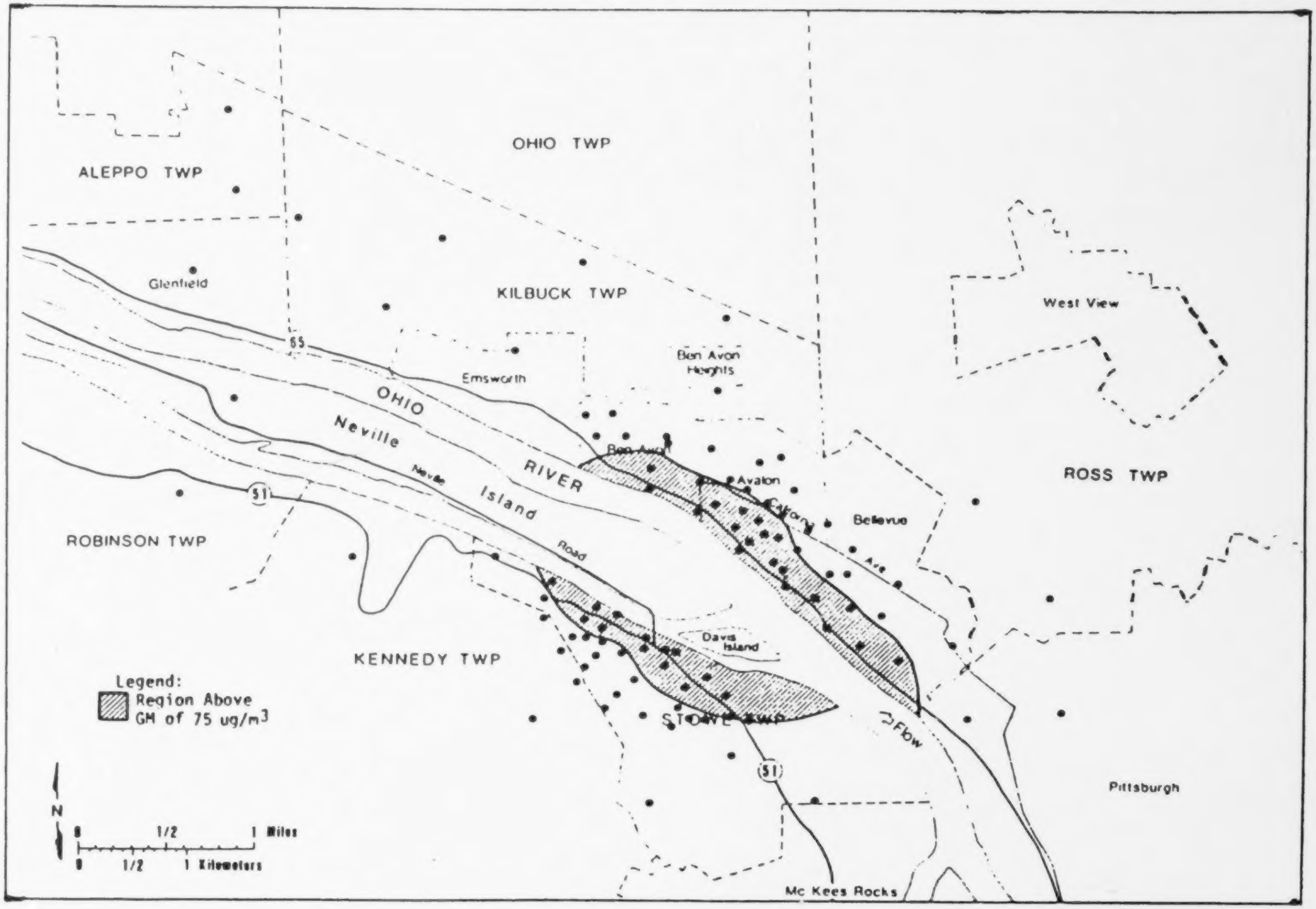
KILBUCK TWP
ALEPPO TWP
ROBINSON TWP
KENNEDY TWP
STOWE TWP
ROSS TWP
West View
Pittsburgh
Bellevue
Avalon
Ben Avon Heights
Ben Avon
Emsworth
Glenfield
OHIO RIVER
Neville Island Road
Davis Island
Flow
Mc Kees Rocks
65
51
Legend:
▲ Avalon BAPC Monitor
● Bellevue BAPC Monitor
1/2 1 Miles
1/2 1 Kilometers
N

Figure 4. Receptor Locations


ALEPPO TWP
OHIO TWP
Glenfield
KILBUCK TWP
West View
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Road
Ben Avon
Avalon
Bellevue
Ave
ROSS TWP
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ROBINSON TWP
KENNEDY TWP
Davis Island
STOWE TWP
Flow
Pittsburgh
Mc Kees Rocks
Legend:
Region Above GM of 75 ug/m3
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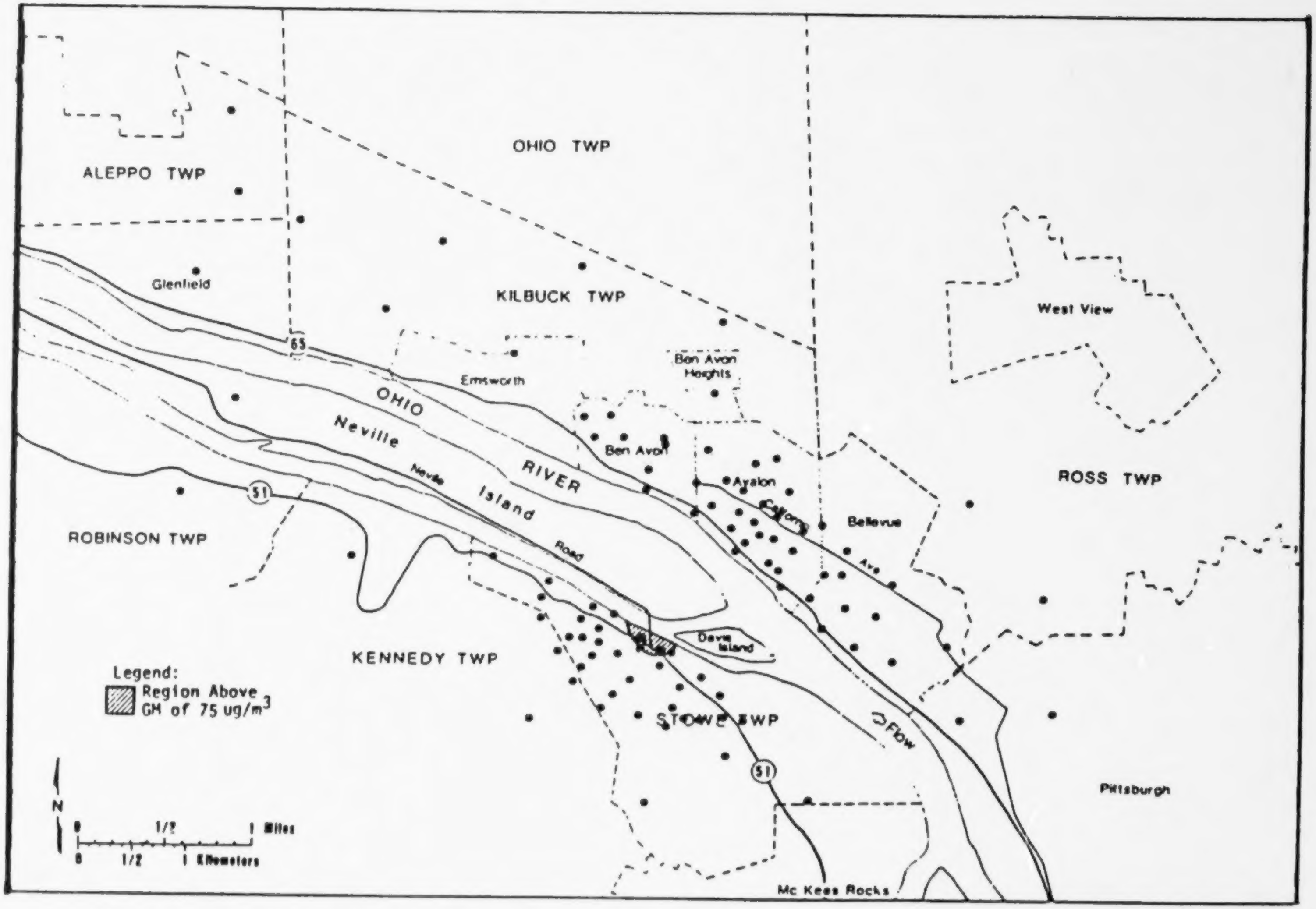
0 1/2 1 Kilometers

Figure 5. Region Within Area 3 Estimated to Have Exceeded the Primary Annual Standard of 75 μg/m³ for Total Suspended Particulates in 1979


ALEPPO TWP
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Ben Avon
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ROSS TWP
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RIVER
Neville
Neville
Island
Road
Davis Island
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51
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ROBINSON TWP
KENNEDY TWP
STOWE TWP
Flow
Pittsburgh
Mc Kees Rocks
Legend:
Region Above GM of 75 ug/m3
N
0
1/2
1 Miles
0
1/2
1 Kilometers

Figure 6. Region Within Area 3 Expected to Remain as Non-Attainment for Total Suspended Particulates in 1982 After Implementation of the State Implementation Plan

For paved and unpaved roads, the emissions were reduced by 80 and 70 percent, respectively, from the base year 1979. This allowed an approximate 6 to 1 trade of road dust for the blast furnace casthouse. A total emissions reduction of 244 tons per year is achieved under the AERO.

Results of modeling using the AERO emissions inventory showed no violations of the annual NAAQS for TSP for any receptor. The highest concentration at any receptor was 72.8 $\mu g/m^3$.

CONCLUSION

Through the use of a validated model, an area can be brought into attainment. However, in situation such as this with complex terrain, it is imperative that cooperation by the local, state and federal agencies be solicited. As a result of this program, an area specific air quality model was validated that served to show how to bring that area into attainment. The validated model also can serve as a tool for agency evaluation of any new or modified source applications for that area.

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CHARACTERIZATION OF SLAG EMISSIONS AT A BLAST-FURNACE CASTHOUSE

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ABSTRACT

Until recently, it was not realized that slag emissions could make a significant contribution to casthouse fugitive emissions as measured by the visual-emission-opacity test. Use of flame or steam to prevent the air oxidation of metal vapors above the surface of molten iron at a blast-furnace casthouse has been highly successful in controlling the metal oxide fumes. However, these noncapture fume-suppression techniques have been ineffective in reducing the emissions from above molten slag. A program was undertaken to physically and chemically characterize the fumes from molten slag to provide a basis for the development of emission-control methods.

Fume samples were collected as aerosols on a membrane filter above the surface of molten slag flowing in a slag runner. Scanning-electron microscopy, Fourier-transform infrared spectroscopy, X-ray-fluorescence analysis, X-ray diffraction, and microchemical analysis involving atomic-absorption spectroscopy and ion chromatography were used to characterize the samples. Although it was determined that the slag-fume solids can be of varying composition, they are composed principally of sulfur oxide derivatives of alkali metals of which potassium is predominant. Specific compounds that have been identified include potassium bisulfate, potassium sodium sulfate, and, tentatively, potassium thiosulfate.

At a casthouse equipped with flame-suppression devices on the iron-transfer areas, statistical analysis of measured visual-emission opacities indicated a correlation with slag composition. There was a direct relationship with lime content, lime-to-silica ratio, and slag basicity. An inverse relationship was found with silica and potassium oxide contents. A mechanism is proposed that relates the behavior of potassium within the blast furnace to the slag-emission observations.

INTRODUCTION

Emission-suppression devices based on the use of a shroud of both flame and steam above molten iron and slag have been installed at a blast-furnace casthouse to control fugitive emissions by a noncapture technique. Visual-emission-opacity (VEO) measurements (1) of the fugitive emissions from this casthouse revealed that, while such techniques are highly effective in reducing emissions from the molten iron, compliance with applicable visual-emission regulations had not been consistently achieved, apparently because of fumes from the molten-slag-transfer areas. Until the development and successful application of flame- and steam-suppression devices to prevent the formation of the reddish-brown iron oxide fumes at the iron-transfer areas, it was not realized that the light-colored and low-mass slag emissions would have a measurable impact on casthouse fugitive emissions as measured by the VEO test. The mechanism by which flame or steam suppresses fuming of molten iron is by the reduction of the amount of oxygen available to the iron surface, thus eliminating the generation of iron oxide and manganese oxide as fume (2). However, it appears that the fume released from the slag-transfer areas may be generated by some mechanism that is not primarily air oxidation because flame suppression had no detectable effect on the control of emissions from molten slag. Therefore, for the development of slag-fume control techniques it was necessary to chemically and physically characterize the slag emissions so that the slag fuming mechanism could be determined. A literature survey yielded no information on the nature of the fumes obtained from molten blast-furnace slag.

A sampling program at a blast furnace with a relatively constant burden composition and a daily iron production capacity of 3800 tons was initiated to provide slag-fume samples for characterization by various analyses. Samples of fume were collected on a membrane filter about 4 feet above the east-taphole slag runner of the blast furnace during casting. The sampling point is shown in Figure 1, a schematic diagram of the casthouse runner arrangement. Flame suppression was used to eliminate metal-oxide fumes from the trough area, iron runner, and hot-metal cars.

EXPERIMENTAL PROCEDURES

SCANNING-ELECTRON MICROSCOPY (SEM)

Aerosol samples were collected over the slag runner and east taphole on Nuclepore polycarbonate 0.8-micrometre (μm)-pore-size filters for analysis by SEM. These samples were collected over periods of 5 to 30 minutes.

A section of each filter was analyzed by SEM energy-dispersive X-ray spectroscopy (EDS). An EDS spectrum was obtained from a 4-millimetre (mm)-square area on each filter. This technique measures the relative atomic abundances of all elements heavier than neon (atomic No. 10). Elements such as carbon, nitrogen, and oxygen cannot be detected. The striking feature of these spectra (Figure 2) is that the predominant elements found on these filters are potassium and sulfur. The X-ray absorption and fluorescence

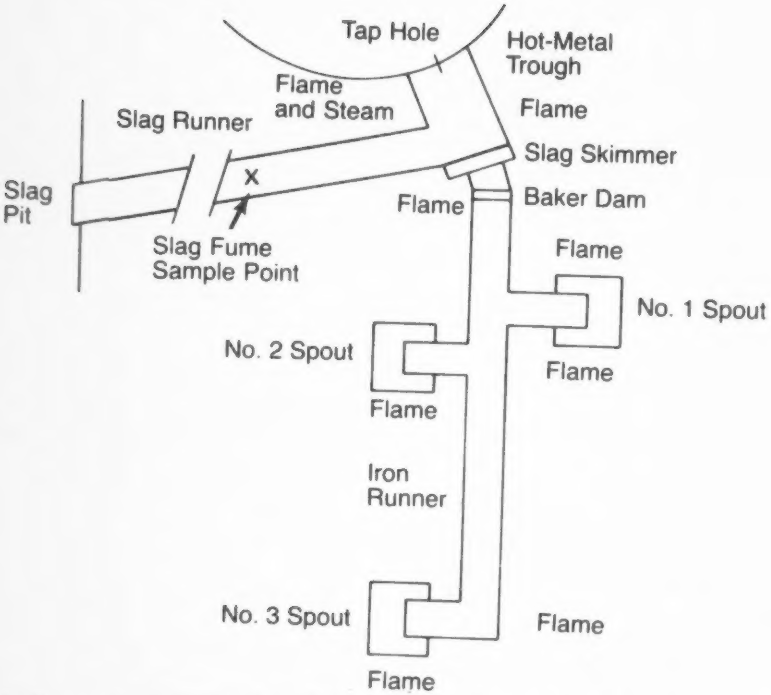
Tap Hole
Hot-Metal Trough
Flame and Steam
Slag Runner
Flame
Slag Skimmer
Slag Pit
X
Flame
Baker Dam
Slag Fume Sample Point
Flame
No. 1 Spout
No. 2 Spout
Flame
Flame
Iron Runner
No. 3 Spout
Flame
Flame

Figure 1. Runner arrangement and slag-fume sampling point at a blast-furnace casthouse.

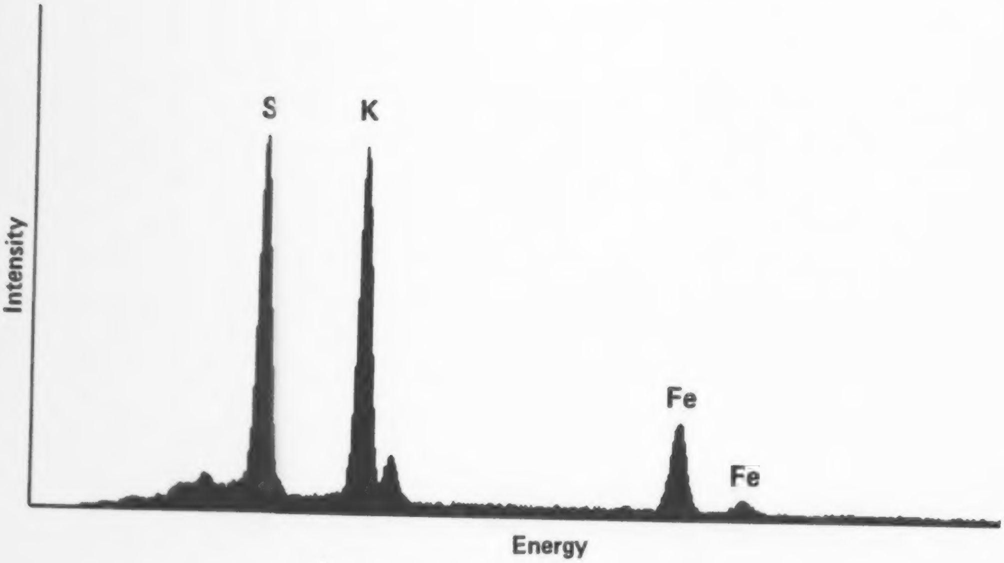

Figure 2. X-ray spectrum of slag-fume solids.

factors are small for these potassium-sulfur compounds, thus the relative elemental X-ray peak areas are a measure of atomic abundance. The EDS method exhibits a reduced sensitivity to particles larger than about 1 µm. For these samples with predominantly submicron particles, the method should provide a good measure of the composition of particles responsible for visual opacity, inasmuch as the small particles make the greater contribution to opacity.

High-magnification SEM micrographs showed the potassium-sulfur material to be in the form of small (ca. 0.1- to 0.5-µm diameter) particles with smooth surfaces. The iron-containing particles are typically larger (ca. 1 to 5 µm) and spherical. EDS spectra and photomicrographs of individual particles showed the iron to be concentrated in particles that are iron (oxide) containing very little potassium or sulfur, whereas the potassium-sulfur particles had no iron associated with them. The atomic potassium-to-sulfur (K/S) ratio for each sample is given in Table 1. The data indicate an average K/S ratio of 1.0. For reference, potassium sulfate has a K/S ratio of 2.0, whereas the K/S ratio for potassium bisulfate is 1.0. There are numerous other possible compounds, and other analytical techniques have been used to identify the specific chemical species present on the filters.

Table 1. SCANNING-ELECTRON MICROSCOPY ANALYSES OF SLAG FUMES

SEM No.	Potassium/Sulfur Ratio	SEM No.	Potassium/Sulfur Ratio
2245	1.0	2254	1.1
2247	1.0	2255	0.8
2248	1.0	2267	0.8
2249	1.0	2268	1.5
2252	0.7	2269	0.9
2253	1.2	2270	0.8
2271	0.9	2281	0.9
2272	0.8	2282	0.9
2276	0.9	2283	1.0
2277	1.1	2284	1.0
2279	1.8	2285	1.3
2280	1.0	2287	1.2

Average 1.0

CHEMICAL ANALYSES

Typically, only about 1 to 5 milligrams of fume samples could be collected on a membrane filter during an entire cast that lasted, on the average, about 45 minutes. This required the development of micro methods to obtain a chemical characterization of the fumes. After several attempts, a procedure based on a combination of atomic-absorption spectroscopy and ion chromatography was developed. For the wet-chemical analysis, Millipore Fluoropore (Teflon) membrane filters (0.2-μm pore size, 47-mm diameter) were found to be satisfactory and did not produce the high blank values that had been obtained when Alundum thimbles were used to collect the fumes. Some tests were made with 0.8-μm-pore-size polycarbonate filters, but the Fluoropore filters were preferred for the chemical work-up because of greater ease of sample manipulation.

When a fume sample on a Fluoropore filter was received, it was cut in half and each section was weighed. One portion was extracted with dilute hydrochloric acid and analyzed for the metallic cations by atomic-absorption spectroscopy. The second half was extracted with water and analyzed for anions such as sulfate, fluoride, and chloride by ion chromatography. The extracted halves of the membranes were dried and weighed to obtain the weight of the sample by difference.

Analyses of two different slag-runner-fume samples are presented in Table 2. The major components are iron, potassium, and sulfate. The atomic K/S ratios were 0.95 and 1.23.

Table 2. CHEMICAL ANALYSES OF SLAG-RUNNER FUMES

	Sample A		Sample B	
	Wt %	Atomic Ratio[a]	Wt %	Atomic Ratio[a]
Lithium	0.03		0.15	
Sodium	3.11	0.25	2.56	0.24
Potassium	21.0	1.00	17.8	1.00
Calcium	0.42		0.51	
Magnesium	0.16		0.12	
Iron	6.85		6.93	
Manganese	0.21		0.22	
Sulfate	54.3	1.05 (as S)	35.5	0.81 (as S)
Fluoride	0.0		0.06	
Chloride	0.18		0.05	
Total[b]	86.3		63.9	

[a] Calculated with K = 1.00.

[b] Samples contained varying amounts of insoluble material believed to be composed mainly of iron oxide and carbon (kish).

Three spoon samples of molten runner slag were taken at the blast furnace on separate days to obtain more complete analyses (Table 3) than are normally obtained on production samples. The data indicate that over 90 percent of the sulfur in the slag is present as sulfide. There are small amounts of sulfate present, but this sulfate may have formed by air oxidation of sulfur species after the slag had left the furnace taphole.

Table 3. BLAST-FURNACE RUNNER-SLAG ANALYSES

Component	Weight Percent		
	Sample C	Sample D	Sample E
Manganese	0.33	0.27	0.25
Silicon	17.3	17.83	17.78
Aluminum	4.48	4.31	4.59
Calcium	30.66	30.15	30.31
Magnesium	4.11	4.26	4.08
Iron	0.62	0.50	0.25
Zinc	0.004	0.003	0.004
Titanium	0.19	0.17	0.20
Fluoride	0.20	0.19	0.16
Chloride	0.01	0.02	0.02
Lithium	0.009	0.009	0.011
Sodium	0.23	0.16	0.13
Potassium	0.41	0.34	0.21
Total Sulfur	1.63	1.52	1.62
Sulfide	1.47	1.40	1.46
Sulfate	<0.01	0.022	0.012

SCANNING-AUGER ANALYSES

To obtain additional information on the chemical composition of the slag fumes, the material collected on the membranes was analyzed by an X-ray-fluorescence technique with the use of a scanning-Auger multiprobe analyzer. With a thin-window detector, the unit is capable of analyzing elements above atomic No. 6 (carbon). In particular, because this technique can measure oxygen directly, it could be helpful in determining whether the oxygen is present in the fume sample as collected, or as a result of hydrolysis or oxidation in the work-up for the chemical analysis of these samples.

The scanning-Auger X-ray analyses (Table 4) indicate that potassium, sulfur, and oxygen are the major components present in the slag fume solids collected on the membrane sampling filters. The K/S ratios for three fume

Table 4. X-RAY ANALYSES OF SLAG EMISSION SAMPLES WITH SCANNING-AUGER MULTIPROBE

Sample	Membrane	Atomic Concentration, %							Atomic Ratios			
No.	Area No.	Fe	K	S	Si	Al	Na	O	K/Na	K/S	O/S	O_c/S[a]
F	1	4.6	17.3	13.7	2.2	0.6	3.0	58.5	5.8	1.26	4.27	3.44
	2	6.8	17.8	14.3	2.5	0.6	3.6	54.4	4.9	1.24	3.80	2.65
	3	3.6	17.4	13.5	2.1	0.2	2.7	60.4	6.4	1.29	4.47	3.79
								Av.	5.7	1.26	4.18	3.29
G	1	5.8	15.0	15.3	2.6	1.3	1.8	58.1	8.3	0.98	3.80	2.82
	2	2.3	13.7	14.2	0.6	0.2	1.7	67.4	8.1	0.96	4.75	4.42
	3	2.8	12.8	14.4	1.4	0.5	1.8	66.3	7.1	0.89	4.60	4.10
								Av.	7.8	0.94	4.38	3.78
H	1	4.2	11.0	10.0	4.8	0.3	2.2	67.5	5.0	1.10	6.75	5.19
	2	3.9	12.3	11.0	4.3	0.3	2.0	66.2	6.2	1.12	6.02	4.72
	3	5.2	12.3	11.1	4.0	0.4	2.0	65.0	6.2	1.11	5.86	4.46
								Av.	5.8	1.11	6.21	4.79

[a] Oxygen values associated with sulfur are corrected (O_c) by assuming that the following metal oxides are present: Fe_3O_4, SiO_2, and Al_2O_3.

samples from different casts were 1.26, 0.94, and 1.11 (average of 1.1). This agrees with the SEM results, which had indicated an average K/S ratio of about 1. An attempt was made to calculate the atomic oxygen-to-sulfur (O/S) ratio, but a correction had to be made for the oxygen present as the metal oxides. For the purpose of the correction calculation, it was assumed that silicon and aluminum are present as silica and alumina. Independent X-ray-diffraction analyses and optical microscopy indicated that the iron is present mainly as magnetite (Fe_3O_4). The corrected O/S ratios for the three samples were 3.29, 3.78, and 4.79 (average of 3.95). This result tends to confirm the chemical analyses results (Table 2) that the oxygen associated with the sulfur is present predominantly as sulfate ion (O/S ratio = 4.0) in the fume solids collected on the filters. The potassium-to-sodium (K/Na) ratios were 5.7, 5.8, and 7.8. The wet chemical analyses (Table 2) gave a 4:1 K/Na ratio on two different samples.

FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Samples of the slag fume solids were examined by Fourier-transform infrared spectroscopy. This technique has the capability of repetitively scanning a sample surface and accumulating low-intensity infrared spectra in computer memory for later generation of an enhanced spectrum. Fume samples collected on polycarbonate and Teflon membranes were examined in this manner, but it was found that background absorption from the membrane materials interfered with the sample spectrum. It was then determined that a small quantity of the solids could be transferred and combined in a potassium bromide pellet so that the infrared spectrum could be accumulated from the pellet. The resultant infrared spectrum indicated that the fume solids contained sulfate and bisulfate species.

X-RAY-DIFFRACTION ANALYSES

Samples of the slag fumes were examined by X-ray-diffraction analysis. To provide an identifiable X-ray-diffraction pattern, the sample components must be crystalline and the particles should have an adequate crystallite size. Iron was found to be present in all the samples as magnetite. Three potassium-sulfur compounds were identified: potassium bisulfate, potassium sodium sulfate, and, tentatively, potassium thiosulfate. All three compounds were not present in each of the five samples examined. X-ray-diffraction patterns indicate that all samples contained additional components that have not been identified. It is of interest that all three of the potassium-sulfur compounds identified have a 1:1 K/S ratio. Attempts to identify potassium sulfate (K_2SO_4, K/S ratio = 2) were made, but no X-ray evidence for its presence was obtained.

STATISTICAL ANALYSIS OF VISUAL-EMISSION OPACITIES

To obtain an insight into the causes of the emissions from molten slag, correlation coefficients were calculated among the visual-emission opacities and variables such as furnace operating parameters, hot-metal chemistry, and slag chemistry. A total of 23 variables was included in a statistical study of 54 casts during a 2-1/2 month period for which VEO data were available for the furnace. The opacity measurements were summarized and used in two ways. In the first method, the average of all VEO readings for the entire cast (Average VEO) was used. In the second, only the VEO readings taken after the start of slag flow from the taphole were averaged over the remainder of the cast. This is defined as "Slag VEO" and should be more meaningful than Average VEO in the present investigation of causes of slag emissions. The Slag VEO readings also include some emissions other than those derived from the slag. These are the iron-derived fumes from the trough and iron-runner areas that escape the fume-suppression devices and the surge in emissions from plugging of the taphole at the end of the cast.

The correlation coefficients were determined by a simultaneous technique at a 95 percent confidence level to identify any linear relationships between either Average VEO or Slag VEO and the other variables. The results of the statistical analysis are given in Table 5. The data indicate that there are no significant correlations with Average VEO, but that there are five slag-chemistry variables that show a statistical relationship with Slag VEO. Direct relationships were found between Slag VEO and lime content, lime-to-silica ratio, and slag basicity and inverse relationships were found with the silica and potassium oxide contents of the slag.

Table 5. STATISTICAL CORRELATION OF VISUAL-EMISSION OPACITIES AND BLAST-FURNACE VARIABLES

Variable	Mean	Standard Deviation	Minimum	Maximum	Correlation Coefficient With Average VEO	Correlation Coefficient With Slag VEO
Top pressure, psi	7.4	0.8	5	8.6	-0.084	-0.123
Top temperature, F	285	80	100	460	-0.118	-0.134
CO/CO_2 ratio	1.42	0.11	1.11	1.59	-0.077	-0.095
Av. hot-metal temp., F	2720	33	2635	2800	0.221	0.252
Second hot-metal temp., F	2729	33	2640	2810	0.271	0.277
Flame temp., F	3699	139	3460	3956	-0.043	0.073
Hot-metal analysis, wt %:						
Silicon	0.96	0.24	0.49	1.70	0.195	0.310
Sulfur	0.033	0.010	0.010	0.059	-0.054	-0.140
Phosphorus	0.074	0.016	0.047	0.102	-0.087	0.058
Manganese	0.73	0.09	0.55	0.96	0.127	0.199
Chromium	0.075	0.020	0.030	0.120	-0.094	0.032
Slag CaO/SiO_2 ratio	1.13	0.06	1.00	1.37	0.308	0.463[a]
Slag basicity, $(CaO + MgO)/SiO_2$	1.38	0.07	1.21	1.64	0.333	0.479[a]
Slag analysis,[b] wt %:						
SiO_2	38.31	1.25	34.11	41.69	-0.320	-0.479[a]
CaO	43.44	0.97	41.70	47.18	0.309	0.447[a]
Al_2O_3[c]	8.9	0.5	-	-	-	-
MgO	9.35	0.49	8.17	10.77	0.106	0.054
S	1.21	0.18	0.90	1.69	0.312	0.283
K_2O	0.47	0.20	0.10	0.88	-0.353	-0.430[a]
MnO	0.28	0.23	0.001	1.04	-0.256	-0.320
Slag volume, lb/THM	634	30	601	751	0.007	0.082
Average VEO, %	11.7	3.7	4.5	22.2	-	-
Slag VEO, %	14.4	4.3	6.0	29.2	-	-
VEO class (1 = fail; 0 = pass)[d]	0.796	0.41	0	1	-	-

[a] Indicates a significant correlation between the variable and Slag VEO at a 95 percent confidence level.

[b] Metal analyses are reported as the oxides.

[c] Al_2O_3 not correlated because of lack of precision in analysis; values are only reported to the nearest integer.

[d] There were 43 casts with opacity exceedances and 11 casts in compliance.

DISCUSSION

The positive correlation of Slag VEO and the three lime-related variables could be interpreted as a function of reactions involving calcium and potassium species in the furnace. The potassium enters the furnace from the coke or ore, mainly as some complex form of potassium silicate. Thermodynamic considerations (3,4,5) indicate that of all the potassium compounds that may exist in the high temperature region of the furnace, potassium silicate is among the most difficult to reduce to potassium metal (boiling point of 766°C). Such high reduction temperatures (1300 to 1550°C) are only encountered in the bosh and hearth areas where the following reactions may take place:

$$K_2SiO_3 + C \rightarrow 2K + SiO_2 + CO \qquad (1)$$

$$K_2SiO_3 + CO \rightarrow 2K + SiO_2 + CO_2 \qquad (2)$$

However, in the presence of lime, an exchange reaction may take place:

$$K_2SiO_3 + CaO \rightarrow K_2O + CaSiO_3 \qquad (3)$$

The chemical activity of alkali oxides dissolved in slag is increased by increasing the basicity of the slag (5). In the reducing atmosphere of the furnace, the potassium oxide is rapidly reduced to potassium metal:

$$K_2O + C \rightarrow 2K + CO \qquad (4)$$

It is well established that the buildup and recycle of potassium inside a furnace can be regulated, to some extent, by lowering the basicity of the slag $[(\%CaO + \%MgO)/\%SiO_2]$ through control of the amount of available lime and/or magnesia.

The negative correlation of Slag VEO with silica may be explained by the fact that silica is considered an acidic component of slag and, in effect, it neutralizes the lime and makes it less available for reaction with potassium silicate.

We considered it significant that there is a negative relationship of Slag VEO with the potassium content of the slag. These results suggest that in casts with lower slag emissions, there are factors involved in a chemical interaction that suppress the loss of potassium species to the air. Conversely, the statistical study suggests that when the potassium in the slag is in a form that is loosely held, the loss of potassium will increase inside the furnace as the slag is formed and descends, and as a result, the potassium content of the slag will decrease. Because a portion of the potassium in the slag as it leaves the furnace taphole will still be in a loosely-held state, there will be more of this potassium species available for vaporization into the casthouse atmosphere and thus increase the VEO. At this point it is not clear whether the interaction is primarily a chemical effect or a physical relationship or a combination of both.

During the period of blast-furnace operations covered by these studies, the potassium content of the burden charge remained constant at 3.8 pounds of potassium oxide per ton of hot metal. Furnace performance data also indicated that there were no unusual problems of buildup of deposits of potassium compounds within the furnace. Estimates of potassium losses as fume in the casthouse, calculated from the measurement of the total mass of particulate fugitive emissions (6), are not of sufficient magnitude to affect the potassium analysis of the slag. This suggests that the chemical interactions involving potassium loss from the slag must also be operating within the furnace on a much greater scale. Potassium compounds can leave the furnace stack as volatile or entrained species in the top gas, or can be deposited on the furnace walls as a relatively intractable solid. Work is in progress to identify factors involved in this relationship between potassium-loss and slag-emission rates in the casthouse.

Fukutake and co-workers (7) developed an empirical relationship for the vaporization rate of potassium from slag within the blast furnace, based on slag basicity, temperature, and surface area per unit mass of slag. Of the various factors evaluated in that study, it was determined that slag temperature had the greatest effect on potassium vaporization rates. Because of this, it was anticipated in the statistical analysis that slag emission outside of the furnace would be positively related to hot-metal temperature, but no strong correlation was found. Casual observation of casts made at widely different hot-metal temperatures suggests that there should be a direct relationship between temperature and slag emissions, but the statistical analyses of the VEO data do not reflect this. The reason for this absence of correlation is not apparent at this time. It may be that the temperature range encountered is too narrow (mean hot-metal temperature of 2729°F and a standard deviation of 33°F) to be significant, and that the database was not large enough to demonstrate a temperature effect.

The chemical characterization evidence suggests that the slag fume may be formed by a reaction between potassium species and sulfur oxides to form a transient intermediate that has not yet been identified. Whether the reaction takes place in the slag after it leaves the taphole or whether it takes place above the slag surface is not clear. Visual observation indicates that the slag emissions form an attached plume which suggests that the fume is already formed as it leaves the slag surface.

One purely speculative possibility is that the transient fume intermediate is potassium pyrosulfate, which can be formed by a number of possible pathways from potassium, potassium oxide, or potassium sulfate by reactions involving either sulfur trioxide or sulfur dioxide and oxygen. It is well known that potassium pyrosulfate is easily hydrolyzed in the presence of water to form potassium bisulfate, which has been identified in the fume sample:

$$K_2S_2O_7 + H_2O \rightarrow 2KHSO_4 \tag{5}$$

Because potassium bisulfate does not have the thermal stability to persist in the molten-slag environment and there is probably no readily available hydrogen source at the slag surface, it appears likely that it is formed at the membrane-collection surface. The potassium bisulfate could undergo additional reactions on the membrane surface because of further contact with reactive species, such as sulfur dioxide, sulfur trioxide, oxygen, and moisture that are present in the air above the slag runner. A complex mixture of potassium-sulfur compounds has been observed on the collection-membrane surface.

CONCLUSIONS

The flame and steam fume-suppression techniques that were developed for molten iron have no detectable effect on the fumes evolved from the slag-transfer areas. To assist in the development of slag-fume-suppression strategies, it is necessary to determine the chemical composition of the fume and elucidate the mechanism by which it is formed. A number of analytical techniques were used to characterize slag-fume samples obtained during casting at a blast furnace.

Scanning-electron microscopy and X-ray-fluorescence analyses indicate that potassium, sulfur, and oxygen are the major components, that the K/S ratio is close to 1.0, and that iron is present in all samples as discrete particles not associated with either potassium or sulfur. Iron is found as iron oxide in all of the slag-fume samples, but is believed to be present due to cross contamination from stray fumes that escape the flame-suppression devices at the trough, iron runners, and hot-metal cars. Chemical microanalyses confirmed the K/S ratio of 1 and suggested that the sulfur was present mainly as sulfate ion. X-ray analysis for oxygen confirms that the sulfate is present in the fume sample, as collected on the membrane, and is not an artifact of the chemical work-up. Fourier-transform infrared spectroscopy showed the presence of sulfate and bisulfate ions. X-ray-diffraction analyses confirmed the presence of magnetite, potassium bisulfate, potassium sodium sulfate, and, tentatively, potassium thiosulfate. Except for the magnetite, none of these species were identified in all of the samples. The samples all contained additional compounds that have not been identified. It is significant that the identified potassium compounds have a K/S ratio of 1. Because of its stability as a vapor at high temperature (8), potassium sulfate (K/S = 2) was specifically looked for in the fume samples, but no evidence for its presence was found.

The collected fumes are a mixture of sulfur oxide derivatives of the alkali metals, predominantly potassium. It is proposed that the slag fumes are being generated from an as yet unidentified common intermediate compound that leads eventually to products with a 1:1 atomic ratio of potassium to sulfur. Secondary reactions of this intermediate with reactive species in the atmosphere above the molten slag surface and at the membrane collection surface lead to the complex mixture of compounds observed.

Correlation coefficients were obtained between the VEO measured during the slag flow and 23 blast-furnace variables. It was found there was a statistically significant direct correlation of Slag VEO with the lime content of the slag, lime-to-silica ratio, and basicity. The relationship of slag emissions with the lime-related factors and the silica content reflects the availability of potassium for conversion to a volatile species both within and outside the furnace. There were inverse correlations with the silica and potassium oxide contents of slags. The negative correlation of Slag VEO with the potassium content of the slag indicates that there are potassium-stabilization factors that can suppress slag-fume generation. Studies to identify slag emission-suppression factors are continuing.

ACKNOWLEDGMENTS

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A LOOK AHEAD - SELECTED ENVIRONMENTAL POLICY DECISIONS

by

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ABSTRACT

Observations are provided on Agency considerations of four complex subjects related to the Clean Air Act. The subjects are emissions trading (bubble), particulate matter, toxics, and Clean Air Act amendments.

The information in this document has been funded, wholly or in part, by the U.S. Environmental Protection Agency. It has been subjected to the Agency's peer and administrative review, and has been approved for publication.

Thank you. It's a pleasure for me to be here today to provide you with some of the flavor of the Washington scene. I have, for a long time, believed that meetings such as this one provides all of us, regulator, industry representative, State and local Government Agencies, environmentalists, and other interested and affected parties, with an opportunity to review and discuss potential environmental actions in a free and open manner.

While most of the speakers during the past two days have addressed specific technical developments and requirements, I see my role here as one of providing some observations bearing on Agency policy considerations. I will limit my remarks this afternoon to 4 complex subjects related to the Clean Air Act.

- Bubble Policy
- PM Standard
- Toxics
- Clean Air Act Amendments

As you are all aware, the Agency has recently undergone a major shift in its management which will quite likely provide some new perspectives in the environmental arena. This Administration has strong, stated commitments to environmental values. Mr. Ruckelshaus recently re-affirmed these commitments, going so far as to alert industry leaders to the possibility of tougher pollution laws than had been previously considered. However, the Agency is fully aware of the need for reasonable and equitable regulatory actions which industry can implement and thereby assure a safe and healthy environment for its neighboring communities.

With respect to EPA's Bubble Policy, in April of last year, the Agency published its proposed Emissions Trading Policy. This document replaces the 1979 Bubble policy, providing interim guidance to the States in processing alternative control approaches for existing sources to meet the NAAQS. The statement expands on the opportunities for applying more efficient control alternatives; more efficient in the sense that they can provide added flexibility to industry, which in turn can result in reduced compliance costs and earlier compliance dates. Since the publication of the interim Policy Statement, EPA has approved or proposed approximately 36 bubbles with significant cost savings.

I don't propose to bore you with the details of the proposed Emissions Trading Policy Statement since it is a matter of public record. (FR 47-15076, April 7, 1982)

However, as a result of that publication, numerous comments were received and specific issues were raised. On August 31, 1983, EPA requested further comments on these issues.

The issues cover such concerns as; what is the definition of "shutdown" and should emission reduction credits be allowed from shutdowns in non-attainment areas requiring, but lacking, demonstrations of attainment?

The current Policy does not explicitly define "shutdown," since credits from shutdowns for use in existing-source bubbles are treated no differently than credits produced by other means of emission reduction. For example, the Policy's discussion of double-counting (where the state may have already taken credit for a partial or complete shutdown as part of its SIP) focuses only on determining the extent to which a particular shutdown is surplus, a requirement for all credits. Under the current Policy, so long as the reduction from a shutdown is enforceable, quantifiable and permanent, as well as surplus, it is eligible for credit.

More precise definition is needed if shutdowns are to be subject to special requirements for use in bubbles. Issues raised by that potential approach include whether "shutdowns" should cover all production cutbacks or curtailments; whether the shutdown must be of an entire plant or only identifiable pieces of process equipment; and whether credit should be based on the surrender of operating permits or some other action. Such distinctions could have major impact, since a broad definition would subject more bubble trades to special requirements.

To help evaluate the effects of adopting any special treatment of shutdowns, comments have been requested on the appropriate definition of "shutdown."

Several alternatives have been identified for resolving the question of credits in non-attainment areas:

° Where RACT has not already been defined in the SIP, require a "negotiated RACT" baseline before shutdowns can receive credit in any non-attainment areas requiring but lacking demonstrations of attainment -- even areas with attainment extensions beyond 1982.

° Require a substantial air quality improvement, beyond a RACT baseline, from each bubble, whether using shutdown credits or not, in non-attainment areas requiring, but lacking, demonstrations of attainment. E.g., require each such bubble to produce for example a 20% net reduction in emissions beyond RACT equivalence.

° The most restrictive alternative, of course, would be to prohibit use of shutdown credits for existing-source bubbles in non-attainment areas requiring, but lacking, demonstrations of attainment.

° The comment period for this notice has been extended to October 31. EPA will then review the responses and plans to publish the final Emissions Trading Policy as part of an overall guidance document for states to use in implementing their SIP programs.

The second environmental issue I want to review with you today is the proposed revision to the National Ambient Air Quality Standard (NAAQS) for particulate matter.

The current standard was promulgated more than 10 years ago in April 1971. The indicator selected at that time was "Total Suspended Particulates" or TSP. Health effects data developed since then has made it clear that TSP is not the most appropriate indicator for particulate matter, especially with respect to the primary standard, since it includes substantial quantities of large particles which are of lesser concern when considering health effects.

This standard has been under intensive Agency review for the past several years. Draft versions of criteria document revisions have been made available for external review and comment. The Clean Air Scientific Advisory Committee (CASAC) held three public meetings to consider each of the developing drafts. A staff paper, developed by OAQPS, was also publicly reviewed. Meetings have been held with Senate and House Staff personnel and representatives of industry and environmental groups to discuss the many issues involved in the studies.

At this point in time, after evaluating, digesting and balancing all of the diverse inputs provided to us as a result of each of these meetings, the Agency plans to propose a new particulate indicator, PM_{10}, for the revised primary NAAQS. PM_{10} includes only those particles having an aerodynamic diameter smaller than, or equal to, a nominal 10 micrometers. We have received recommendations suggesting that other indicators might be more appropriate than PM_{10}. For example, a smaller size cutoff equivalent to a PM_6 indicator has been suggested. In the proposal the Agency will request comments and data that might possibly support a different indicator for the health-related primary standard.

The present TSP indicator is a mass standard where larger particle sizes dominate the concentration measurement. While the proposed PM_{10} indicator is also a mass measurement parameter, it emphasizes the smaller particles, those known to be a direct contributor to respiratory diseases.

With respect to the secondary standard for particulate matter, the Agency is considering retaining the TSP indicator but with the level of the standard based upon an annual geometric mean value rather than the current 24 hour standard. This would tend to focus control efforts on larger urban areas, which are of principal concern, rather than on more rural areas. However, no final decision has been made regarding the size cut or level.

When the PM standard is proposed, the Agency will issue an updated control technology document (CTD) for the States' use in the implementation, or revision, of their SIP and for PSD actions. Also, the existing NSPS covering particulate matter will be reviewed and revised if necessary.

Turning now to still another area of priority effort at EPA - air toxics. Although there are several Agency options for acting on toxics or hazardous substances, the principal authority for controlling toxic air pollutants is Section 112 of the Clean Air Act. Section 112 provides for the establishment of National Emission Standards for Hazardous Air Pollutants or NESHAPS.

Once a pollutant has been identified as hazardous, the various emission sources are evaluated to determine which should be regulated under Section 112. This assessment includes the number of sources in a given category, the quantity of emissions, emission concentrations and the number of people exposed. The next level of assessment is concerned with health effects, considering both individual risks and aggregate risks, as well as identifying the available technology to control the emissions.

In the case of hazardous pollutants that are known carcinogens, EPA takes the position, shared by other Federal regulatory agencies, that in the absence of sound scientific evidence to the contrary, these pollutants should be considered to pose some cancer risk at any exposure level. However, in determining the appropriate level of regulatory requirement, the cancer risk is qualitatively balanced with consideration of control technologies, control costs, and the public health benefits associated with the operation of affected facilities. Since the risk factor is a calculated parameter, subject to uncertainties, this balanced consideration is necessary. The current Section 112 regulatory process results in the application of BAT (Best Available Technology) to control hazardous emissions. Once BAT has been applied then the residual risk is assessed to determine if controls beyond BAT are required.

Some concerns have been raised relative to the determination of BAT for emission controls that are based in part on the economic feasibility of installing available technology.

In the recent regulatory proposal for arsenic, the Agency requested public comments on the degree to which information on exposure and public risks should be used to establish BAT. As a result of several requests, the public comment period on this proposal has been extended to December 10th after which the Agency will review the docket submittals, prior to preparing a final promulgation package.

I should point out that the Agency's concerns with risk assessment and risk management criteria is pervasive and has the priority attention of the Administrator.

Several efforts are currently underway which explore both inter- and intra-Agency risk activities. An intra-Agency task force is currently reviewing the various risk and exposure assessment criteria for a variety of toxic substances being addressed by several offices within the Agency. Additionally, the Administrator has taken the lead in establishing an inter-Agency task force on asbestos and in a broader sense, he is discussing the establishment of an inter-Agency policy group to coordinate all toxics regulation. This activity would also cover the issues of risk assessment and risk management.

At this point let's turn to a discussion of the Clean Air Act and the possibility of Amendments to the Act being enacted this year. As you are all aware, revisions to the Clean Air Act have been a subject of Congressional debate for the past three years. In March of this year, Senator Stafford introduced a comprehensive set of Clean Air Act amendments which were identical to those reported last year. However, last year's bill did not gain sufficient support from the Senate, the Administration nor environmental groups for any final action to be taken. Action on this year's bill, or any alternate bill, will probably not occur until the Clean Air Act re-authorization hearings in both the House and Senate are held later this year.

While the Administration has indicated that, at this time, it is not contemplating proposing a comprehensive bill of its own, the Administrator has initiated a series of task force studies that will provide the background for any new legislative initiatives the Agency may decide to take.

Two such initiatives relate to acid rain and sanctions for non-attainment of the ambient air quality standards. The Administrator has not yet announced the results of the task force options study on acid rain which would include the Agency's recommendations for both short and long term actions to mitigate this environmental problem. Additionally, the Administrator has developed a policy statement related to the sanctions provisions contained in the Clean Air Act. This policy is currently in the Agency's final review process and should be available shortly.

In conclusion, the Agency is moving out on several fronts to implement effective and meaningful approaches for carrying out the intent of the Clean Air Act. I look forward to your help in meeting the nation's commitment to provide its citizens the clean air they have clearly indicated that they want.

METHOD FOR DETERMINING PARTICULATE MASS EMISSIONS FROM IRON AND SLAG RUNNERS

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ABSTRACT

Techniques for the local control and suppression of casthouse emissions have shown promise as an economical alternative to full casthouse evacuation. Quantification of emission reductions achieved through these measures, however, requires knowledge of the mass-emission rate from the uncontrolled source. Unfortunately, the fugitive nature of fume-generating activities in an uncontrolled casthouse makes measurement by known standard procedures impractical, and thus requires the development of specialized techniques. U. S. Steel Research has developed a test procedure for the determination of emission rates from iron and slag runners that utilizes a specially designed fume-collection system and standard Method 5 equipment. Emission factors in terms of pounds per hour per square foot of runner surfaces can be determined by this method. The design and operation of the portable fume-collection system are discussed and the details of actual field measurements are reported. The reduction of the field data to emission factors for both iron and slag runners is also presented. Finally, the reliability of these measurements is assessed by appropriate statistical techniques.

INTRODUCTION

Reported estimates of emissions from uncontrolled blast-furnace casthouses range from 0.2 to 0.6 pound per ton of hot metal (lb/ton),(1)* as measured by Environmental Protection Agency (EPA) Method 5.(2) These emission factors are typically determined for the aggregate exhaust fume, including taphole, trough, runner, and spout emissions as measured at the baghouse inlet for the casthouse having a full-house evacuation-control system. Thus, assignment of emission factors on an individual source basis was not possible. Because much attention is presently focused on the local control and suppression of individual fume sources within the casthouse, determination of specific source emission factors would be useful in determining overall casthouse emission-control strategies. These factors might also be useful in the development of bubble trade-offs for the casthouse.

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* See References.

Accordingly, a measurement procedure, which utilizes a specially designed fume-collection system, has been developed for the determination of iron- and slag-runner emissions. Emission factors in terms of pound of particulate per hour per square foot of runner surface may be determined by this method. With knowledge of runner lengths and flow duration, emission factors in terms of pound per ton of hot metal (lb/ton) may also be calculated. An initial series of measurements demonstrating this technique was successfully performed at the USS Duquesne Plant No. 6 blast furnace in 1982 and emission factors have been calculated. Subsequent to these measurements a replicate series of measurements were taken in 1983. The newly developed procedure is suitable for the determination of runner emission factors for casthouses of any runner configuration.

EXPERIMENTAL METHOD

To quantify runner emissions for the Duquesne No. 6 blast furnace, emissions from a known uncontrolled runner segment were captured with a portable hood and fan and measured in a 14-inch-diameter circular duct using EPA Method 5. A diagram of the runner-emission measurement system is presented in Figure 1. A flow-control damper was installed on the exhaust side of the 4000-actual-cubic-foot-per-minute fan to facilitate adjustment of the null capture flow. Null flow exists when the hood face velocity is maintained near the fume rise velocity, thus permitting collection of a representative sample over the defined runner segment.

An initial velocity traverse was performed from two 90-degree opposed sampling ports located eight-duct diameters downstream from the hood to determine flow conditions. In view of the flat undisturbed velocity profile present, it was elected to perform emission measurements isokinetically at a single average velocity point.

The collection hood was designed with a 13-inch by 36-inch rectangular opening and support pads to allow placement directly over the iron or slag runner. Mineral wool insulation was applied to all interior hood surfaces prior to testing and successfully prevented thermal warping during the test.

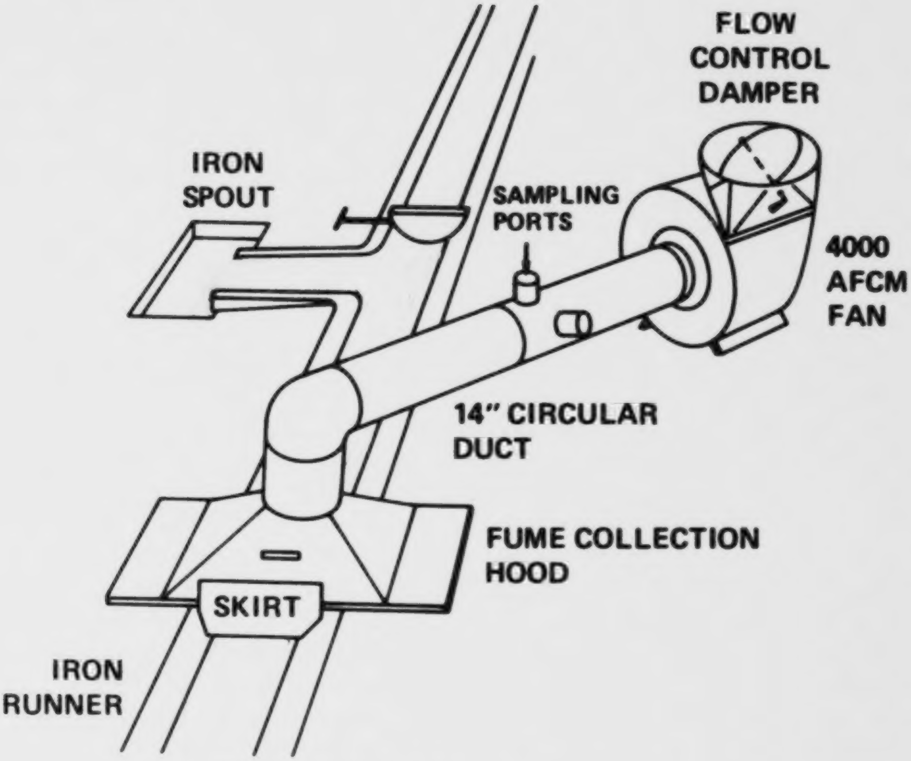

Figure 1. Runner emission-measurement system.

The No. 6 blast furnace has two independent tapholes and runner systems. Due to safety considerations, measurements could only be performed on the east system, which has 184 feet of iron and slag runners. A diagram of the east runner system is presented in Figure 2. Measurements performed on the east side are considered to be representative of the west runner system also because of the similarity of the runner systems. The average runner cross section was approximately one foot wide at the slag or hot-metal surface and 2-1/2 feet wide at the level of the casthouse floor. Slag or hot-metal surfaces were typically one foot below the casthouse floor. For measurement of emissions from hot-metal the collection hood was located over a segment of the main runner between the Baker dam and the No. 1 spout. This allowed collection of fume for the longest duration because all hot metal passed this runner segment enroute to the spout. Slag-runner measurements were made at a location approximately 20 feet downstream from the iron trough. Visual inspection of runner fume during the survey indicated that fume quantities generated at both of these sample segments were representative of their respective runner. Any variation in emission rate between the sample segment and the iron-runner section between the second and third spouts would have little influence on the calculation of total

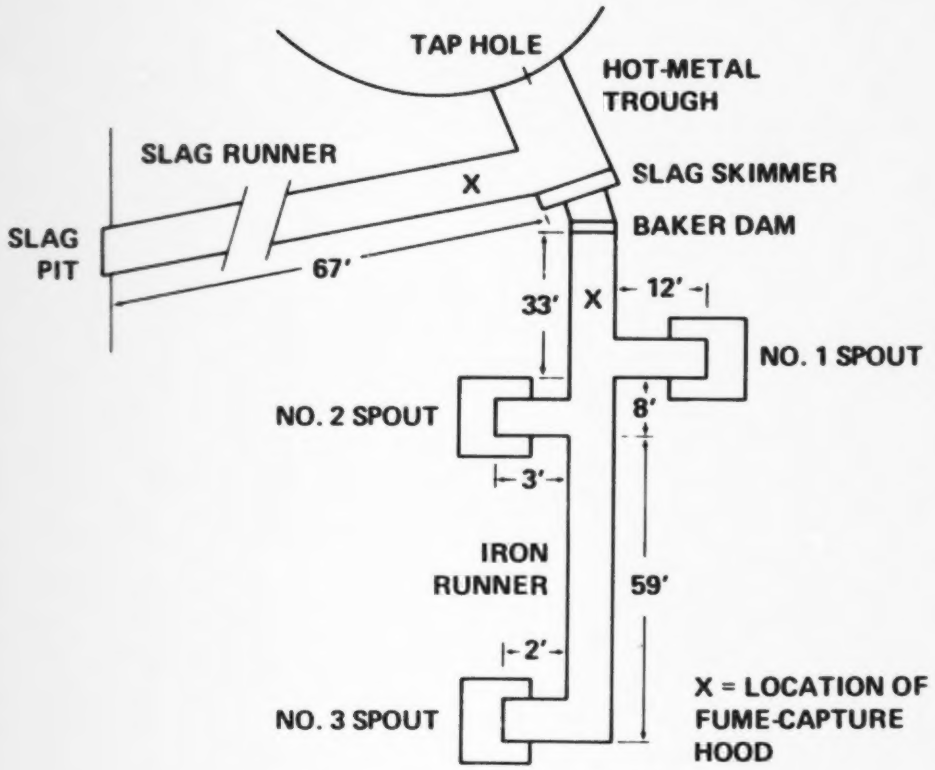
TAP HOLE
HOT-METAL TROUGH
SLAG RUNNER
X
SLAG SKIMMER
BAKER DAM
SLAG PIT
67'
33'
X
12'
NO. 1 SPOUT
NO. 2 SPOUT
8'
3'
IRON RUNNER
59'
2'
NO. 3 SPOUT
X = LOCATION OF FUME-CAPTURE HOOD

Figure 2. Duquesne No. 6 blast-furnace east runner system.

casthouse emissions because of the short iron-flow duration to the third spout.

A volume flow rate in excess of 2000 standard cubic feet per minute (scfm) was required on initial trial runs to adequately capture runner emissions. These runs were not considered acceptable, however, since a gap of one foot or more between the hood and hot metal permitted entrance of extraneous fume into the hood. During strong-wind conditions, the channeling of fume along the runner and into the hood was particularly acute. To help alleviate this interference, two 1/8-inch steel-plate skirts were fabricated and suspended from the sides of the hood to a distance of within several inches from the hot metal. Through careful damper adjustment and sealing of the hood skirts, null capture flows in the range of 800 scfm were attained for later measurement runs. The above flow translates into an average hood face velocity of about 200 feet per minute (ft/min), which is roughly equal to the estimated fume-rise velocity above the runner. A fume-capture segment, measuring approximately 20 inches by 12 inches, was defined by the distance between the two skirts and the width of the runner stream. Length and width measurements were recorded for each trial. However, runner widths were sometimes highly variable during a particular cast and should only be considered as approximations.

A total of 9 acceptable hot-metal-runner and 13 acceptable slag-runner measurements was performed over both measurement periods. Measurement commenced with the flow of molten slag or iron under the hood and concluded shortly after the plugging of the taphole. The average time of measurement was about 40 minutes. All field work and laboratory analyses were performed in accordance with EPA Method 5 with the exception of the aforementioned average sampling point within the duct.

In addition to the determination of mass emissions, samples of iron- and slag-runner fume were also obtained from the measurement duct for characterization by scanning electron microscopy—automatic image analysis.

During each run, flow duration per runner section was recorded for use in calculating total emissions in pounds per ton of hot metal, lb/ton. Hot-metal chemistry and temperature information were secured from the furnace cast sheets, and an estimate of total tons of iron per cast was made by Duquesne operating personnel.

RESULTS

Dust loading in units of pounds per hour (lb/hr) was calculated for each run as the product of dust concentration and duct flow volume. Runner-emission factors in pound per hour per square foot of runner surface ($lb/hr/ft^2$) were calculated for the iron and slag runners, by dividing dust loading values by the appropriate runner surface area. For the first series of measurements average uncontrolled runner emission rates of 1.02 and 0.33 $lb/hr/ft^2$ were determined, respectively, for hot-metal and slag. For the second series, slag emission rates averaged 0.31 $lb/hr/ft^2$ while hot-metal emission rates decreased to 0.65 $lb/hr/ft^2$. This decrease, however, is not statistically significant. The combined average emission rate for the uncontrolled iron runner was 0.90 $lb/hr/ft^2$. These results are presented in Tables I and II. Values for hot-metal tests 1 through 4 and slag-runner test 1 were not reported due to excessive fume infiltration from outside the designated runner-sampling segment.

For purposes of calculating runner emissions in lb/ton, individual dust-loading values were first divided by the length of the runner segment sampled to yield an emission factor in pounds per hour per foot (lb/hr/ft). This procedure assumes uniform runner width at any given time over the entire runner system during the cast. By applying these factors for each trial in conjunction with runner length and flow duration, an average total runner-emission factor of 0.15 lb/ton was estimated for all tests. By applying the appropriate statistical techniques, we are 95 percent confident that the true value lies within ±0.05 lb/ton of the estimated value. The contribution from iron alone was 0.11 lb/ton or nearly three times that of slag, which contributed 0.04 lb/ton. It should be noted that the implementation of fume

TABLE 1. DUQUESNE NO. 6 BLAST-FURNACE RUNNER-EMISSION MEASUREMENT HOT-METAL-RUNNER RESULTS

Trial No.	Duct Temp., °F	Flow, scfm (dry)	Dust Conc., gr/scfd	Dust Loading, lb/hr	Runner-Emission Factor, lb/hr/ft^2	Total Runner Emissions, lb Ton Hot Metal
			1982 Series			
5	333	812	0.134	0.93	0.98	0.10
6	255	895	0.354	2.7	1.8	0.16
7	260	858	0.190	1.4	0.92	0.17
8	320	805	0.124	0.86	0.65	0.070
9	210	737	0.082	0.52	0.89	0.056
10	397	601	0.284	1.46	0.91	0.079
Average			0.195		1.02	0.11
			1983 Series			
1	243	705	0.173	1.04	0.60	0.08
2	300	742	0.143	0.91	0.54	0.11
3	300	761	0.215	1.40	0.80	0.12
Average			0.177		0.65	0.10
Average All Runs			0.189		0.90	0.11

TABLE 2. DUQUESNE NO. 6 BLAST-FURNACE RUNNER-EMISSION MEASUREMENT SLAG-RUNNER RESULTS

Trial No.	Duct Temp., °F	Flow, scfm (dry)	Dust Conc., gr/scfd	Dust Loading, lb/hr	Runner-Emission Factor, lb/hr/ft^2	Total Runner Emissions, lb Ton Hot Metal
1982 Series						
2	267	788	0.062	0.42	0.36	0.030
3	306	1069	0.086	0.79	0.47	0.085
4	274	792	0.077	0.52	0.32	0.041
5	242	843	0.049	0.35	0.19	0.030
6	200	719	0.096	0.59	0.52	0.034
7	356	684	0.096	0.56	0.37	0.055
8	288	746	0.070	0.45	0.29	0.039
9	270	766	0.058	0.38	0.24	0.039
10	200	861	0.054	0.40	0.25	0.034
Average			0.072		0.33	0.04
1983 Series						
1	240	915	0.087	0.68	0.39	0.05
2	272	816	0.080	0.56	0.32	0.04
3	308	763	0.070	0.46	0.26	0.04
4	318	648	0.080	0.44	0.25	0.04
Average			0.079		0.31	0.04
Average All Runs			0.074		0.33	0.04

suppression technology has almost completely eliminated iron runner emissions. Because these techniques are ineffective in the control of slag runner emissions, an investigation into the mechanism of slag fume formation is in progress and should lead to the development of acceptable slag fume suppression techniques. Runner-emission-factor sample calculations, based on average and individual test values, are included in Appendix A.

Scanning electron microscopy—automatic image analysis (SEM-AIA) was performed on two iron and two slag fume samples.(3,4,5) This technique furnishes information on size distribution by weight based on individual particle size and density. These data were used to calculate a weight distribution based on aerodynamic equivalent diameters. These data are summarized in Figure 3 as a plot of aerodynamic diameter versus cumulative percent by weight less than stated size. From these curves, it can be seen that in both cases 98 percent of the fume weight was derived from particles with aerodynamic diameters of under 130 microns (µm). A 130-µm unit density, spherical particle will attain a terminal setting velocity of about 100 feet per minute at standard conditions in still air.(6) Because this velocity is well below the estimated fume-rise velocity and hood face velocity of 200 feet per minute, it is concluded that nearly all sampled fume would remain airborne and exit the casthouse.

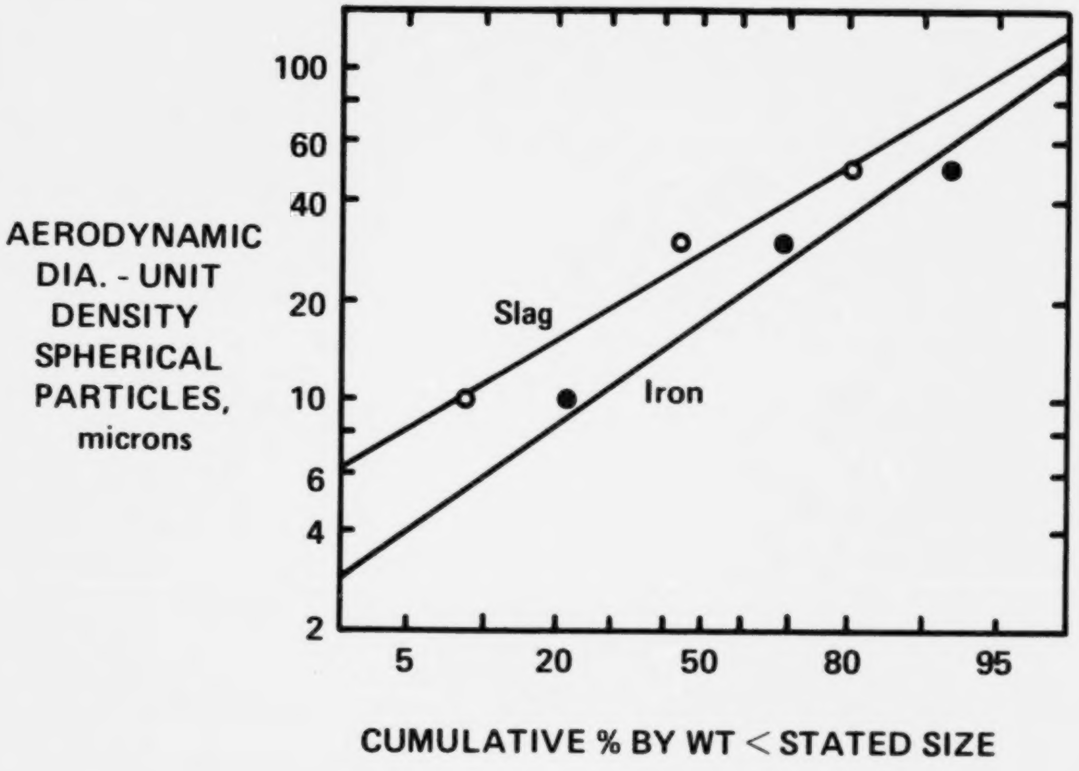

Figure 3. Particle-size distribution of fume from slag and iron runners.

Iron temperature and slag and iron chemistry data are tabulated in Tables 3 and 4 on a trial-by-trial basis. Any effect that changes in these parameters may have had on emission rates is not readily identifiable. Due to the large number of variables and the relatively small number of trials performed, correlation coefficients were not calculated.

TABLE 3. DUQUESNE NO. 6 BLAST FURNACE OPERATING DATA - HOT-METAL-RUNNER TRIALS

Trial No.	Iron Temp., °F	Hot-Metal Analysis, weight percent Si	S	P	Mn	Cr
		1982 Series				
5	2760	1.04	0.019	0.067	0.81	0.09
6	2680	0.79	0.050	0.058	0.74	-
7	2660	0.96	0.035	0.062	0.75	-
8	2640	0.82	0.091	0.048	0.58	0.06
9	2680	0.85	0.073	0.049	0.64	0.07
10	2720	1.16	0.043	0.043	0.70	0.06
		1983 Series				
1	2770	1.38	0.043	0.062	0.78	0.05
2	2725	1.06	0.053	0.067	0.79	0.05
3	2745	1.34	0.048	0.067	0.83	0.05

TABLE 4. DUQUESNE NO. 6 BLAST FURNACE OPERATING DATA - SLAG-RUNNER TRIALS

Trial No.	Iron Temp., °F	Slag Analysis, weight percent SiO_2	Al_2O_3	CaO	MgO	S	K_2O
		1982 Series					
2	2710	38.10	7.77	44.27	9.42	2.02	0.25
3	2750	38.16	7.62	44.93	9.28	1.59	0.29
4	2725	38.43	7.67	43.42	9.11	1.55	0.05
5	2710	38.05	7.48	43.20	9.99	1.50	0.50
6	2760	36.74	8.15	45.08	10.90	1.67	0.10
7	2795	37.10	8.74	44.50	10.42	1.72	0.19
8	2780	36.76	8.49	44.18	10.61	1.64	0.17
9	2695	38.88	8.38	43.28	9.60	1.63	0.37
10	2685	39.13	8.36	43.23	9.34	1.57	0.43

1983 Series							
1	2735	37.85	9.00	44.15	9.01	1.33	0.49
2	2760	39.48	8.00	43.26	9.26	1.35	0.74
3	2730	39.70	8.00	42.41	9.89	1.22	0.52
4	2745	40.38	8.00	41.64	9.98	1.30	0.44

CONCLUSIONS

This study has successfully demonstrated a technique for the measurement of slag- and iron-runner emission rates. A specially designed fume-collection system was used to satisfactorily complete over 20 sample runs at the Duquesne No. 6 blast furnace and sustained no hood damage as a result of the intense radiant heat from the runner. When operated with the aid of fume-deflection skirts, null capture flows in the vicinity of 800 scfm were required for adequate fume capture over the designated runner segment. Particle-size-distribution data indicated that nearly all sampled fume would remain airborne and exit the casthouse if uncontrolled.

In terms of emission-rate-per-unit area, the Duquesne iron runners have a nearly three times greater uncontrolled emission factor than the slag runner. Total runner emissions of 0.15 lb/ton were determined for the No. 6 casthouse by applying these factors over the east runner system. Through the application of current suppression techniques excellent control of fumes from the iron runners is being achieved. Ongoing research into the mechanisms of slag fume formation should lead to the development of suitable techniques for the suppression of slag runner emissions.

The between-trial variations exhibited in the two data sets cannot be readily explained by differences in runner materials, iron temperature, or chemistry. Therefore, more measurements may be needed to establish any such correlations. Additonal studies are being performed to establish a range of emission factors for a cross section of casthouse designs. From a larger database, the variables affecting runner-emission rate may be more thoroughly investigated.

ACKNOWLEDGEMENT

The contribution of J. F. Kelly in determining particle size distribution is gratefully acknowledged.

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APPENDIX A

SAMPLE CALCULATION FOR RUNNER-EMISSION FACTOR CALCULATED ON INDIVIDUAL TEST BASIS

Test No. 2, slag, June 23, 1982

$$\frac{\text{Emissions, lb}}{\text{Runner section}} = \text{(emission rate, lb/hr/ft) (length of runner section to spout, ft) (duration of iron or slag flow in runner section, min.) (1 hr/60 min.)}$$

SLAG-RUNNER EMISSIONS

$$= 0.24 \text{ lb/hr/ft} \times 67 \text{ ft} \times 30 \text{ min.} \times 1 \text{ hr/60 min.} = 8.0$$

$$\frac{\text{Slag-runner emissions, lb}}{\text{Iron cast, ton}} = \frac{8.0}{260} = 0.030$$

Test No. 6, iron, July 2, 1982

$$\frac{\text{Emissions, lb}}{\text{Runner section}} = \text{(emission rate, lb/hr/ft) (length of runner section to spout, ft) (duration of iron or slag flow in runner section, min.) (1 hr/60 min.)}$$

TOTAL IRON-RUNNER EMISSIONS

Emissions to first spout

$$= 1.5 \text{ lb/hr/ft} \times 45 \text{ ft} \times 9 \text{ min.} \times 1 \text{ hr/60 min.} = \quad 10.1$$

Emissions to second spout

$$= 1.5 \text{ lb/hr/ft} \times 44 \text{ ft} \times 17 \text{ min.} \times 1 \text{ hr/60 min.} = \quad 18.7$$

Emissions to third spout

$$= 1.5 \text{ lb/hr/ft} \times 102 \text{ ft} \times 4 \text{ min.} \times 1 \text{ hr/60 min.} = \quad \underline{10.2}$$

Total 39.0

$$\frac{\text{Iron-runner emissions, lb}}{\text{Iron cast, ton}} = \frac{39.0}{240} = 0.16$$

The work described in this paper was not funded by the U. S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

The material in this paper is intended for general information only. Any use of this material in relation to any specific application should be based on independent examination and verification of its unrestricted availability for such use, and a determination of suitability for the application by professionally qualified personnel. No license under any United States Steel Corporation patents or other proprietary interest is implied by the publication of this paper. Those making use of or relying upon the material assume all risks and liability arising from such use or reliance.

FLUID DYNAMIC MODELLING OF ARC FURNACE CHARGING AND TAPPING EMISSIONS

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ABSTRACT

Fluid dynamic modelling has been used to develop solutions to fume capture problems during charging and tapping of a 165 ton electric arc furnace.

Capture of charging fume was simulated by an inverted 1:96 scale model of the meltshop, utilizing the negative buoyancy effects of saline solution in water. Test results show that with modifications to the existing crane and canopy hood, significant improvement of fume capture efficiency is achievable, thereby avoiding large expenditure for expanding fume collection system capacity.

The capture performance of two types of low level tapping hoods, for use where the ladle is held by the crane, was measured using a 1:10 scale model. Air was used as the test medium, with a heat source to simulate the buoyancy driven fume during tapping. Test results show that furnace direct evacuation systems usually have sufficient capacity to capture tapping emissions with this new type of hood.

INTRODUCTION

Most electric arc furnaces have secondary (furnace charging and tapping) emission control systems using canopy hoods. The hoods are located high above the furnaces within the meltshop roof truss structure. By the time the fume reaches the hoods, it is greatly diluted through mixing with clean meltshop air. The large volume flowrate requires fume control system capacities ranging from 300,000 ft^3/min to well over 1 million ft^3/min depending on factors such as furnace size, meltshop geometry and general plant ventilation conditions.

Canopy fume hood capture performances are typically low, in particular, when in-plant cross drafts deflect the plume away from the hood.

Attempts to improve the capture of fume have been traditionally directed towards increasing suction at the hood off-takes. Costs for such retrofit modifications are of the order of \$15/ft^3/min with expenditures of several million dollars for hardly noticable improvements in the capture of fume.

Developing a plant specific fume capture system on the basis of fluid mechanic model tests has turned out to be by far the most cost-efficient way to optimizing secondary emission control. In this case, the recommended plant modifications are estimated to cost only 10% of what they would cost if the same result was to be achieved through an increase in fume system capacity.

MODELLING CONSIDERATIONS

The 2 parameters governing model (m) to prototype (p) scaling are:

the Reynolds No, $Re = \frac{VL}{\nu}$ and

the Froude No, $Fr = \frac{V^2}{Lg \frac{\rho_o - \rho}{\rho_o}}$ where

V = velocity
L = length
g = gravitational acceleration

ρ_o = ambient air density
ρ = flow field density
ν = kinematic viscosity

All units are selected to yield dimensionless parameters. For fluid mechanic scaling purposes it is necessary that:

$$Re_p = Re_m \quad \text{and}$$
$$Fr_p = Fr_m$$

where the variables making up Re and Fr are measured in corresponding locations in the model and the prototype.

The Reynolds number is not a critical scaling parameter because prototype flows are almost always fully turbulent due to large Reynolds numbers in the order of 100,000. Flow patterns are similar in different geometric scales as long as the important flow fields are fully turbulent. It is therefore important to build air models large enough to ensure fully turbulent flows. If the model becomes too large, it is better to use water as a test medium instead of air. Because of the smaller kinematic viscosity of water when compared to air, Reynolds numbers in water are larger therefore permitting the model to be built smaller. Water models on the other hand are usually more costly and more cumbersome to work with.

In this case, tapping fume capture was modelled in a 1:10 scale air model and charging fume capture was simulated in a 1:96 scale water model. The later model consisted of the entire meltshop section housing the furnace. It was inverted because heavy salt water was used to model the rising warm fume plume.

Froude number equality yields the following useful relationships:

$$\left(\frac{V^2}{L\,\frac{\rho_o-\rho}{\rho_o}}\right)_m = \left(\frac{V^2}{L\,\frac{\rho_o-\rho}{\rho_o}}\right)_p$$

$$\frac{V_m^2\ L_m^4\ L_p^4\ \rho_m}{L_m\ (\rho_{om}-\rho_m)} = \frac{V_p^2\ L_m^4\ L_p^4\ \rho_p}{L_p\ (\rho_{op}-\rho_p)}$$

$$\frac{Q_p^2}{Q_m^2} = \frac{L_p^5}{L_m^5}\ \frac{\rho_{om}\ (\rho_{op}-\rho_p)}{\rho_{op}\ (\rho_{om}-\rho_m)} = S^5\ \frac{T_m\ (T_p-T_{op})}{T_p\ (T_m-T_{om})}$$

with $q = Q\,\rho c p\ (T - T_o)$ and $\frac{\rho_p}{\rho_m} = \frac{T_m}{T_p}$:

$$\frac{Q_p^3}{Q_m^3} = S^5\ \frac{q_p}{q_m}$$

where:

- the subscript 0 denotes ambient conditions
- specific heats are assumed constant
- S is the model scale (= 10 for a 1:10 scale model)
- Q is a representative volume flowrate
- T is a representative hot gas temperature
- ρ is the gas density
- q is the heat flowrate

The required prototype flowrate at the hood off-take (subscript 1) is for example:

$$Q_{p1} = Q_{m1}\, S^{5/3} \left(\frac{q_p}{q_m}\right)^{1/3} = Q_{m1}\, S^{5/2} \left(\frac{(T_p - T_{op})\, T_m}{(T_m - T_{om})\, T_p}\right)^{1/2}$$

It is therefore necessary to know either the prototype heat release or a representative gas temperature before the model flowrate Q_m can be scaled up to the prototype flowrate. Fortunately, it is not important to know these variables accurately because they enter into the equation only to the 1/3 power.

The fume hood capture efficiency η is the ratio of pollutant flowrate P_1 captured to the pollutant flowrate P (lb/hr) emitted from the source. Similarity of diffusion of pollutant and heat permits evaluation of η through the identity:

$$\eta = \frac{P_1}{P} = \frac{F_1}{F} = \frac{q_1}{q}$$

where the subscript 1 denotes fume hood off-take conditions. F is the constant buoyancy flux responsible for the plume rise (ref. 1) in ft^4/sec^3 given by:

$$F = \frac{\rho_0 - \rho}{\rho_0}\, g\, Q$$

The total flow of pollutant in a plume is constant, regardless of how much the plume is diluted. The same applies to the flow of buoyancy F simply because the flow of heat is constant. The assumption of relatively small temperature differences permits the very useful simplification:

$$\eta = \frac{(T_1 - T_o)\, T}{(T - T_o)\, T_1} \left(\frac{Vp_1\, T_1}{Vp\ \ T}\right)^{\frac{1}{2}} \approx \frac{t_1 - t_o}{t - t_o} \left(\frac{Vp_1}{Vp}\right)^{\frac{1}{2}}$$

where Vp_1 is a representative velocity pressure in the fume hood off-take. The denominator is constant and proportional to F.

For a typical source-plume-hood configuration, the constant $K = (t - t_o)\, Vp^{\frac{1}{2}}$ is measured by applying ample suction at the hood off-take, therefore ensuring 100% capture. In the above equation the denominator is then equal to the numerator.

Hood efficiency tests are based on t_1 and Vp_1 measurements corresponding to hood suction flowrates of interest. Flowrates are scaled according to the previously referenced equation relating Q_p to Q_m.

The above approach works well for relatively steady emissions as found during furnace tapping. Furnace charging is a highly non-steady state process lasting anywhere from 5 to 15 seconds. The major puff takes typically 3 seconds to rise from the furnace top to the roof truss level. Also, heat releases vary greatly. Flames often engulf the scrap bucket and reach the crane trolley. This happens when scrap containing combustibles is dropped into a liquid steel pool during the second charge.

Models can simulate this process very successfully and it is possible to measure the mean hood capture efficiency very accurately. The method is based on measuring the amount of light transmitted through a sample of the entire pollutant captured during the process. In the equation:

$$\eta = \frac{P_1}{P} = \frac{F_1}{F}$$

a metered amount of heavily dyed salt solution represents both the pollutant P and the buoyancy flux F. The heavy salt water provides the driving force in the inverted model. It corresponds to the hot plume in the field.

The procedure is best described using an example. Let the entire fume capture process take 5 minutes. At the end of this period the hood is clear and any spilled fume is irrecoverably lost. During the corresponding period in the model, let 4 gallons of water be collected from the hood off-take. For 100% collection efficiency these 4 gallons contain all the injected dye, for 50% collection efficiency, they contain half the injected dye. Sample concentrations can therefore easily be generated by injecting known quantities of dyed salt solution directly into 4 gallons of water. A calibration curve of light meter readings versus percent total pollutant contained in 4 gallons forms the basis of the actual tests as shown in figure 4. The method is very accurate, much more accurate than the measurement of field fume collection process parameters serving as input to the analysis.

TAPPING FUME CAPTURE MODEL TESTS

Figure 1 shows a model of the low level tapping hood. The hood is essentially a side draft hood partially extending over the ladle. In this case, it was not possible to place the ladle onto stands or a transfer car because of the excessive spout travel of the furnace during tapping. The ladle has to be lowered during this process. The crane operator's job of keeping the ladle in the correct position with respect to the furnace spout is greatly facilitated by shock absorbing cushioned bumpers acting as hood protectors and guides for the crane hooks.

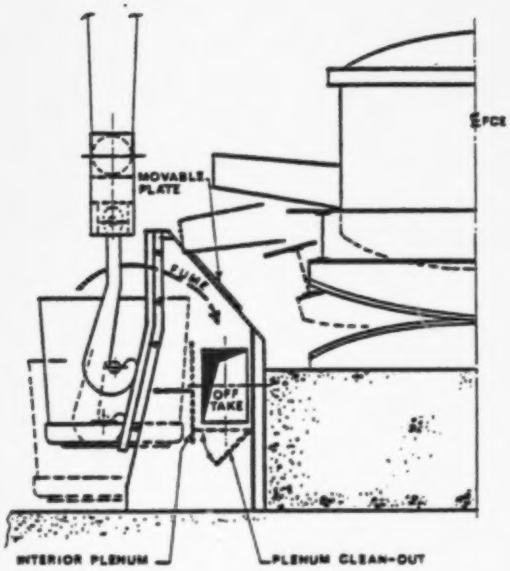

FIGURE 1: LOW LEVEL ARC FURNACE TAPPING HOOD ARRANGEMENT, MODEL 1.

The sloping top of the hood holds a freely sliding plate which is pushed downward by the spout. This permits the spout to protrude into the hood. The hood off-take is connnected through dampers to the furnace direct evacuation system. In the model, the hood was evacuated by a small industrial exhauster in the inlet of which t_1 (°F) and Vp_1 ("WG) were measured.

The ladle model contained a 5,000 BTU/HR (q_m) heating element generating the plume buoyancy. The plume was made visible with the use of fuming titanium tetrachloride.

Tests showed, that the different ladle positions and the simulated changing liquid steel level had a marked effect on fume capture efficiency. Efficiencies were therefore averaged and plotted. The correlation between Q_p and Q_m was established, knowing from prototype plume studies and theoretical ladle heat loss calculations that q_p for a 165 t ladle during tapping is about 30 x 10^6 BTU/hr.

Another more direct and probably more accurate analysis was used to double check the model tests. The plant has existing hoods for tapping fume control for which the off-take suction flowrate was known. The model was therefore used to first simulate the actual field conditions as observed and photographed. This method has been successfully used in the past (ref. 2). The model hood suction was adjusted to give the model the same flow pattern as found in the field. The resulting ratio of Q_p/Q_m was therefore the scaling factor used to test an array of different hood configurations and hood off-take flowrates. The same method was also employed for the charging canopy hood tests.

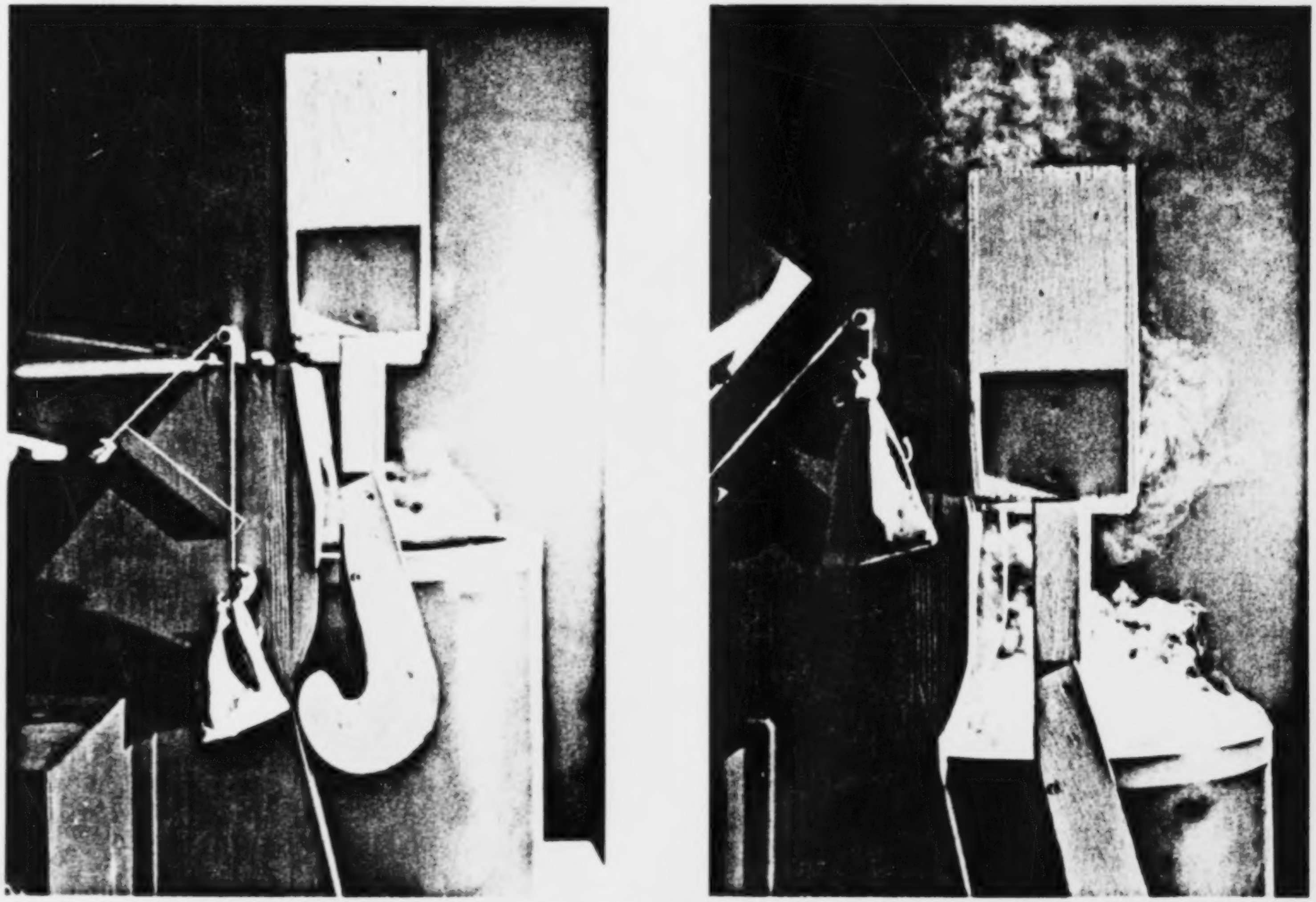

FIGURE 2: TAPPING HOOD MODEL TESTS. LEFT: START OF TAP, CAPTURE EFFICIENCY = 99%.
RIGHT: END OF TAP, CAPTURE EFFICIENCY = 93%.

Figure 2 shows a typical tapping hood test with less than 100% capture efficiency. Figure 3 shows the test results of 2 different low level tapping hood configurations.

For an off-take suction flowrate of 125,000 ft^3/min as available from the furnace direct evacuation system hood 1, the hood shown in figure 1, was found to be about 7% more efficient than hood 2. It should be noted that 97% capture efficiency is much better than what could ever be achieved with large capacity and costly canopy hood systems (these are typically 80% efficient).

The important conclusion from tapping fume collection tests is, that technology is available to capture tapping emissions locally using arc furnace direct evacuation system capacities. Hoods can be built to suit any ladle - furnace configuration regardless of whether the ladle is crane held, resting on stands or carried by a transfer car. Low level tapping fume collection systems capture fume much more efficiently than canopy hoods. The system capital and operating costs are also significantly lower.

CHARGING FUME CAPTURE TESTS

Figure 5 shows the charging fume canopy hood test arrangement. The model includes the following features:

- plant ventilation (air changes) are simulated;
- the important relatively clean hot plume rising from the open furnace and filling the hood before the charge is modelled;
- the significant features of the clam-shell scrap bucket and crane are modelled;
- the existing hood and emission pattern is modelled. The capture efficiency was found to be only 38%.

Early on in the tests it was realized, that any charging fume hood sizing analysis, be it theoretical or in a model must include the dispersion of fume by the scrap bucket and crane. It was found that due to this dispersion no hood could be built to capture the emissions satisfactorily using the available 310,000 ft^3/min system suction capacity. The degree of blockage of the hood by the crane is shown in figure 6. The problem is representative of most steel plants equipped with canopy hoods. Typical charging canopy hood model tests are shown in figure 7.

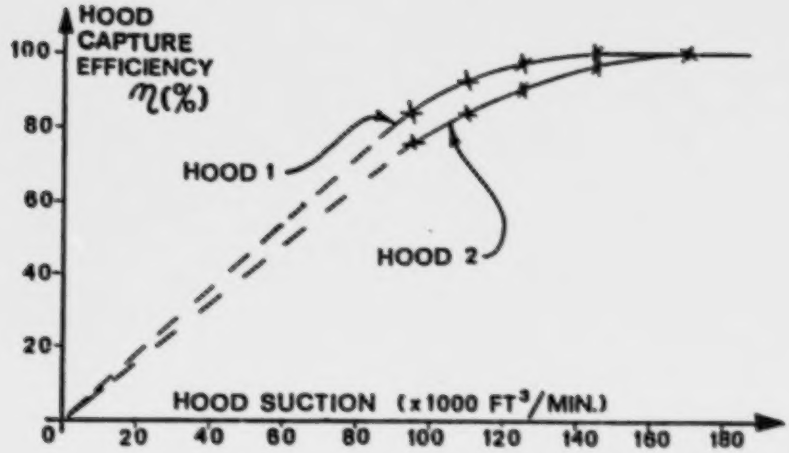

FIGURE 3: TAPPING HOOD MODEL TEST RESULTS

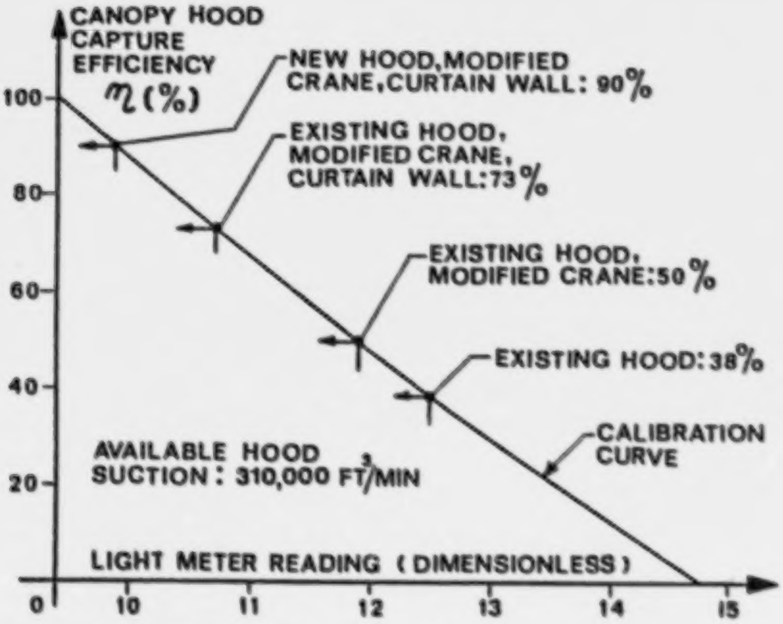

FIGURE 4: CHARGING HOOD MODEL TEST RESULTS

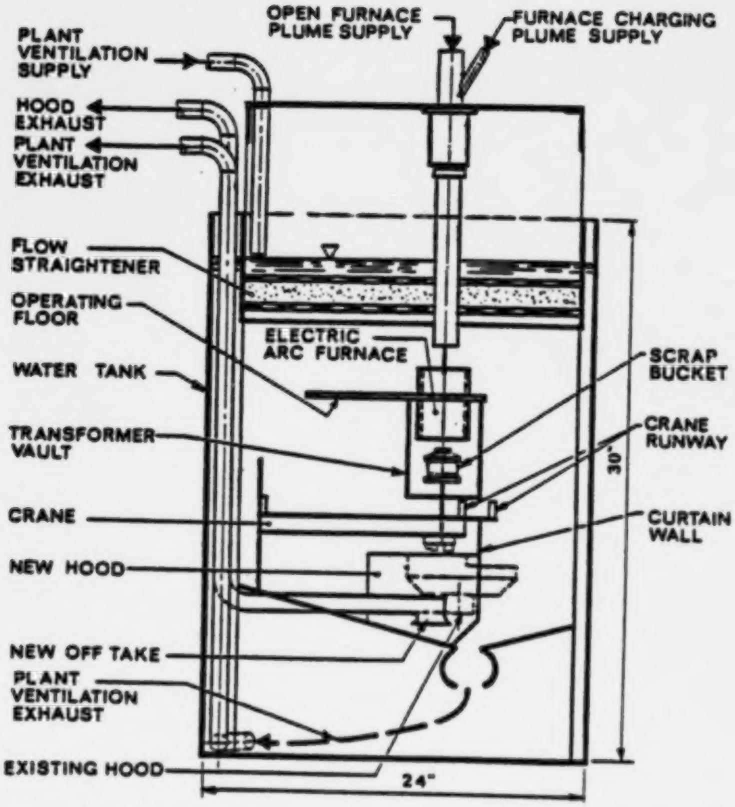
OPEN FURNACE PLUME SUPPLY
FURNACE CHARGING PLUME SUPPLY
PLANT VENTILATION SUPPLY
HOOD EXHAUST
PLANT VENTILATION EXHAUST
FLOW STRAIGHTENER
OPERATING FLOOR
ELECTRIC ARC FURNACE
SCRAP BUCKET
WATER TANK
TRANSFORMER VAULT
CRANE RUNWAY
30"
CRANE
CURTAIN WALL
NEW HOOD
NEW OFF TAKE
PLANT VENTILATION EXHAUST
EXISTING HOOD
24"

FIGURE 5: ARC FURNACE CHARGING CANOPY HOOD MODEL

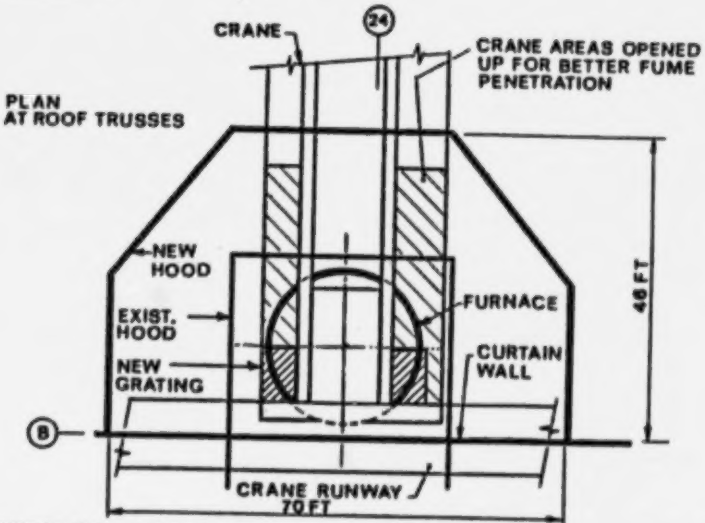
CRANE
24
CRANE AREAS OPENED UP FOR BETTER FUME PENETRATION
PLAN AT ROOF TRUSSES
NEW HOOD
FURNACE
EXIST. HOOD
NEW GRATING
CURTAIN WALL
46 FT
B
CRANE RUNWAY
70 FT

FIGURE 6: CANOPY HOOD AND RELATED CHARGING CRANE MODIFICATIONS

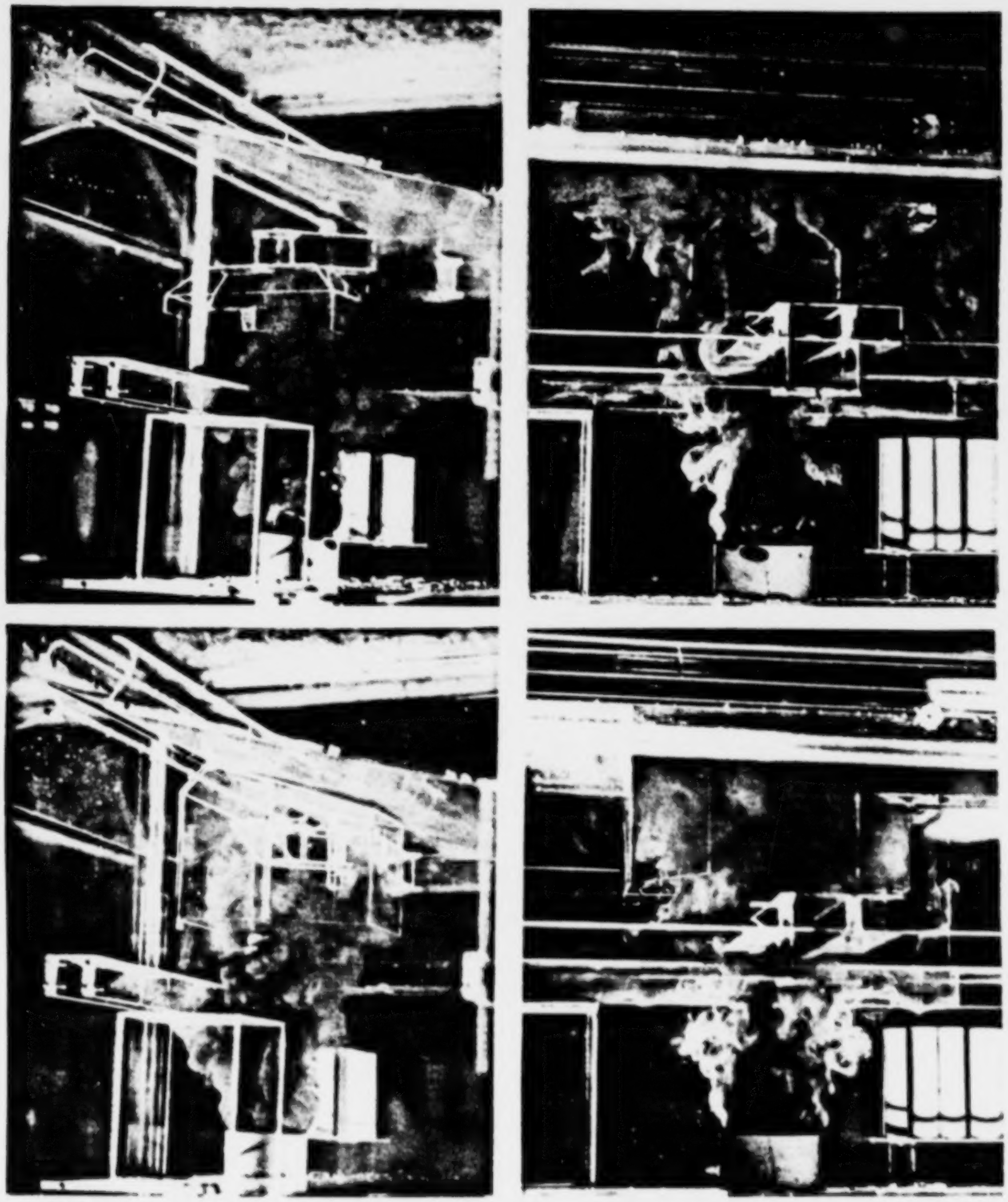

FIGURE 7: CHARGING HOOD MODEL TESTS. LEFT: START OF CHARGE, RIGHT: END OF CHARGE. TOP: EXISTING HOOD. NOTE DEFLECTION OF FUME BY CRANE AND CRANE TROLLEY AND EMISSIONS FROM ROOF MONITOR. BOTTOM: NEW HOOD.

Field inspections and crane supplier inquiries showed that the crane could be modified to permit the fume to rise into the hood with fewer obstructions. The modifications included removal of the switchgear and walkways away from the rising plume (less maintenance). This necessitated an increase in diameter of the crane bridge drive shaft to eliminate bearings and, therefore, the need for access in the area of the hood. Also a narrow emergency cat walk at the top of the crane bridge in the hood area only was added to satisfy safety requirements.

The optimum hood shape is shown in figures 5 and 6. The shape was slightly compromised in order to permit attaching the hood siding to existing trusses. Such a large hood usually causes fume to fall back out of the hood. This can be overcome by installing hood baffles (ref. 1). In this case baffles were not needed because the roof configuration allows placing a very deep hood within the roof truss structure. The hood includes however a curtain wall reaching down to the crane runway. This wall helps reducing the effect of cross drafts and gives lower volume flowrates by reducing entrainment into the plume.

The resulting canopy hood efficiency was measured to be 90% (ref. figure 4). About 10% of the fume impinged on the bottom of the crane runway and was irrecoverably lost to the tapping aisle. A canopy hood efficiency of 90% has to be considered excellent by any standard, in particular, when arc furnace charging fumes have to be captured.

The tests clearly show that relatively low capacity canopy fume hood systems can successfully capture arc furnace charging emissions, provided:

- The hood configuration permits storage of the peak fume burst without overturning and subsequent spillage of fume.

- The charging crane can be modified to do away with switchgear and the associated walkways in the area of the rising plume.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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PRESENT STATE OF THE ART IN COKE PUSHING EMISSIONS CONTROL

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ABSTRACT

Modern clean air requirements, high operating costs, and problems handling the wet sludge from existing control systems led to the purchase of the first land-based fabric filter system to capture coke battery pushing emissions in 1978. Since then there have been several such systems installed or placed under contract. Three different hooding arrangements have been utilized: traveling hood (Minister Stein), single spot (Mitsubishi), and coke side sheds. Three different types of fabric filters, including low ratio shake, reverse air, and pulse jet collectors have been used, both with and without precoat systems. Considerable operating experience has been accumulated on these various systems since the first installations started up in 1979. This paper will attempt to summarize the present state of the art in pushing emission control utilizing fabric filtration and compare the operating experience which has been gained.

This experience was reported in the responses to a special survey of the operating installations. Particular emphasis was placed on problems that have been encountered and their solutions. Some of the more typical problems are: high pressure drop and bag failure caused by condensation and fine particulate, abrasion from coke breeze, corrosion brought on by high moisture and the general atmosphere of the coke battery, and reduced performance caused by improper equipment design. The problems are discussed in some detail, with the specific plants and equipment suppliers remaining anonymous.

Introduction

There have been many significant achievements in the control of air pollution from coke plants and several important papers document this progress beginning with a major specialty conference in Pittsburgh in 1979. One of the more recent papers, "A Comparison of Alternate Coke Pushing Emission Control Systems" by Metzger, et al, outlines the three basic types of collecting hoods and land-based control systems. Since the performance of these three types of collection systems form the basis for this paper, let us briefly describe them for your reference.

1. Traveling hood system, sometimes called Minister Stein: The hood attaches to the quench car and all gases can be collected as the car travels to the quench tower. The top of the main exhaust duct is sealed with a flexible belt which allows the hood to move to any position under suction.
2. A movable hood system: The hood plugs into individual damper ports in the exhaust duct. Arrangements are shown in Figures 1 and 2.
3. A coke side shed covering entire battery: Gases are collected from all of the ovens with emphasis on the oven being pushed.

Although wet scrubbers and electrostatic precipitators have cleaned pushing emissions successfully, high operating and maintenance costs have resulted in the switch to fabric collectors during the last few years. Movable control systems which eliminate long duct runs were good in theory but were found to be awkward and expensive to maintain compared to the more popular land-based systems. Therefore, the emphasis of this paper will be aimed at the design and performance of land-based fabric filter systems.

The first fabric filter began cleaning coke pushing emissions in 1979, and there are now at least 27 coke batteries whose pushing emissions are being controlled by this design in North America. More than one million operating hours have been logged on these fabric filters, and quite a bit has been learned about their design and operation. For this paper we wanted to compile and condense this experience into a form which would be useful to coke plant operators and pushing emission system designers. We have surveyed a number of the installations, and based on this survey, we will attempt to provide an update of how the systems have operated. We will discuss the successes and some of the more significant problems which have been encountered.

For our survey we sent out 31 questionnaires (sample questionnaire is shown in Exhibit 1). Over 90% were returned completed, and we want to acknowledge and thank every one who took the time to respond. Several companies sent articles, papers and write-ups on their systems in addition to our questionnaire.

Operating Experience

We should note at the outset that the majority of the surveyed installations with fabric filters are operating with outlet emission levels well within the EPA and state codes of 0.02 gr/SCF dry. Pressure drops across the fabric usually average 4" to 6" spwg, and operating and maintenance problems in most cases have been no worse than those associated with fabric filters in general. There are some notable exceptions, however, which have led to certain operating problems and dissatisfaction with the collection equipment. In addition, there are implications for design modifications which could be made to existing plants, or incorporated in new plants, to enhance their performance.

The types of operating problems encountered can be grouped into three categories:

I. Basic design problems in: A. Hood System
    B. Fabric Filter
II. Bag plugging and high pressure drops
III. Corrosion

Let's discuss each in some detail:

Basic Design Problems in the Hood System

All three types of hoods, if properly designed, collect pushing emissions adequately, even on green pushes. Typical operating gas volumes are shown below. Note that the gas flow requirements for sheds are roughly twice that needed for traveling or movable hoods.

Traveling Hood	
One spot quench car	100,000 - 150,000 ACFM
Conventional quench car - moving	150,000 - 180,000 ACFM
Hood With Individual Damper Ports	
One spot quench car	100,000 - 150,000 ACFM
Conventional quench car - moving	150,000 - 180,000 ACFM
Coke Side Shed	200,000 - 350,000 ACFM

Many times site-specific factors, such as available space or operator preference, influence the selection of one type of hood over another. Some of the major advantages and disadvantages of the various hoods encountered in our surveyed installations are shown below:

Good Features and Problems with Various Hoods

1. Traveling Hood - Systems in Operation: 7 Batteries

    a. One Spot Quench Car - The hood can follow the quench car to the quenching station. However, before the car leaves the quench tower and re-couples to the hood, ventilation must be stopped to prevent steam from entering the hood and fabric filter.

    b. Conventional Quench Car - This modification offers a potentially cost-effective design concept in retrofit situations since existing cars can be utilized, often without modifications. Since the hood must be designed for a moving car, ventilation volume must be larger than that required for the one-spot car.

    c. Use of a conventional car requires more attention by the operator. In one plant a portion of the gas duct sealing belt was destroyed when a push was caught and the car was not moved. The gas temperature increased until the belt caught fire.

2. Movable Hood with Damper Ports - Systems in Operation: 8 Batteries

    The hood section cannot travel to the quench tower, therefore, more time is required under the hood to allow emissions to subside - especially after green pushes. The conventional quench car option faces the same conditions as those with the traveling hood.

3. Coke Side Shed - Systems in Operation: 12 Batteries

    This is the simplest of all hoods, with few moving parts. However, certain negative aspects have been reported.

    a. The larger gas volume results in $100,000 - $150,000 additional annual operating costs.

    b. Moisture from coke quenching and the coke wharf is often drawn into the fabric filter. This has been a big problem, and has caused bag blinding and corrosion of the fabric filter internals.

    c. The shed catches door leakage, but this may increase the hydrocarbon load to the fabric filter, resulting in more precoat consumption.

    d. Several sheds leak fume out the ends. Depending on the shed design and the ventilation volume, this can be either a continuous problem or one which occurs only when the end ovens are pushed.

Basic Design Problems in the Fabric Filter

Our survey indicates that the following types of fabric filters have been installed:

8" reverse air	2 units
5" shaker	4 units
8" shaker	1 unit
Jet Pulse collectors	20 units

Because they are somewhat less costly to install, the pulse collectors tend to predominate, so we will direct our comments principally to this type of fabric filter. (A typical pulse collector is shown in Figure 3).

The survey seems to confirm that the degree of difficulty for the fabric filter is:

- Inversely related to the coking time. Merchant coke plants with long coking times produce dusts which are easier to handle, while blast furnace coke plants with 18 hour coking cycles have more difficulties.
- Directly related to the moisture content in the gas stream, exhaust gases from sheds cause more problems because of the increased moisture and possibly also because of door leakage.

In general, the dust appears to be easily filtered by the bags, since very low outlet loadings were reported. In some cases, however, the collected dust was quite difficult to pulse off the bags. One of the reasons for this could be an inadequate pulsing or bag cleaning mechanism.

What does this difficulty in removing dust from the bags imply for a "proper design?"

a. Maximum bag cleaning impact force apparently makes the difference. Many design variables can affect impact force, such as:

   - Manifold length: shorter is better than longer; fewer bags per row is better; 15 - 18 bags per row is optimum.
   - Manifold and diaphragm valve size: 1-1/2" diameter appears to be the most successful size. This valve size has been used in several installations and transmits more compressed air and cleaning force than smaller sizes.
   - Manifold hole size: hole air flow area must be large enough to transmit adequate force directly into the center of the bag. In some cases the hole size is varied along the manifold to achieve uniform pulse pressure.

- Bag length: in our survey, bag lengths between 9 & 12 feet were reported. In general, better cleaning is achieved with shorter bags. A length/diameter ratio of 20 - 25 is best on this application.

- Diaphragm valve: a double diaphragm valve was used on several installations and seemed to produce a lower pressure drop than a single diaphragm valve.

b. Air-to-cloth ratio: the old axiom about "never having too much fabric" still applies. Operating air-to-cloth ratios in our survey ranged from 4 - 7 CFM/ft^2 fabric. Based on reported pressure drop and bag life, 7 appears too high. Probably 4 - 6:1 is optimum.

c. Type of fabric: 16 oz. felted polyester was the most successful fabric. Homopolymer acrylic was tried in one installation with limited success. Nomex was used in several units and seemed to perform well when the moisture content was not too high.

In general, a batting of finer denier fibers reduces dust penetration through the fabric, and a thorough silicone treatment improves cake release. The survey responses confirmed that a higher quality felt than a "standard" bag was necessary to achieve satisfactory performance.

d. Gas distribution: several installations suffered premature bag failure due to coke breeze abrasion. Proper gas distribution and a baffled inlet to prevent direct impingement on the bags is important.

High Pressure Drop Problems

Most of the installations are operating in the range of 4" to 6" spwg across the fabric. However, several had bag pressure drops exceeding 8" to 16" spwg. At these levels, the main ID fan(s) often reached maximum capability and ventilation of the hood or shed essentially stopped until the filter bags were replaced.

Bag plugging can be caused either by inadequate design, as mentioned above, or by condensed moisture or condensed hydrocarbons and tars, or other factors, such as extremely fine dust. In general, the fabric filters having a precoat system which injects material directly into each compartment seem to operate better than those with no precoat. They also operate better than those installations with only an "additive" system, which injects the precoat material into the inlet plenum with the hope that this material will be distributd properly.

Figure 4 shows a design of a well conceived precoat system which has been used successfully on several installations. The main feature of this system is that the precoat material is injected into each module in a positive fashion instead of being added in the inlet plenum. This design allows the operator to be sure that the module which has just been cleaned will be properly precoated before being brought back on line.

Bratina, in his 1979 paper, "Fabric Filter Applications on Coke Oven Pushing Operations," discusses the bag protection afforded by a properly applied precoat system. His paper also describes the most effective precoat materials, such as agricultural limestone, coke breeze, pulverized coal, and others. Several of the installations with high pressure drop problems, however, also have some type of precoat system. This finding prompted a closer look at the mechanism of bag blinding which causes this pressure loss. Our studies to date led us to the following tentative conclusions:

a. Precoating the bags seems to protect them quite effectively against blinding by condensed hydrocarbons and tars.

b. If there is high moisture content in the gas stream which is condensing on the bags or there is free droplet carryover, the bags may have a high pressure drop, even with a precoat system.

The worst problems with moisture condensation are in the baghouses after coke side sheds or on systems where the quench car returns under the hood after quenching, and the steam plume goes up into the baghouse. Those installations where the shed covers the coke wharf and receives the moisture and emissions from the quenched coke, seem to have even greater problems. There is some evidence that high pressure drop under these circumstances could be caused by fine particles of chlorides or sulfates from the quenched coke. Of the 10 batteries with coke side sheds and fabric filter gas cleaning systems presently in operation, several have high pressure drop problems. As a generalization, it appears important that the sheds be operated in some way to minimize the amount of moisture plume from the quench car which enters the shed and baghouse.

Corrosion Problems

The atmosphere of a coke battery tends to be highly corrosive to fabricated steel. Any pushing emission control device fabricated mostly of carbon steel, with only special components made of stainless steel, is therefore highly affected by this corrosive atmosphere. This is particularly true of those systems located down-wind of the quenching station. Several installations which we surveyed will require extensive corrosion maintenance after only three years in operation. It is therefore important and cost-effective to consider corrosion protection such as a good surface coating system before operation.

The Major Corrosion Areas Indicated in the Survey Were:

- Inside and outside of baghouse
- Access and supports
- Inside and outside of clean gas duct, fan, stack.
- Outside of dirty gas duct.
- Exterior of all hood and shed systems.

The following practices and material selections seemed to reduce corrosion at several installations:

- galvanized grating
- 304 L SS sheeting on shed
- sandblast and coal tar epoxy coat
- minimize flat surfaces which can collect corrosive dust
- grating in lieu of checker plate to prevent dust accumulation
- SS covers on electrical junction boxes and switches
- corrosion allowance on all steel plate - min. 3/16" preferred on baghouse casing and ductwork
- One company has installed electric heaters and insulation on the hoppers with good results.

Conclusion:

The land-based fabric filters that we surveyed are meeting the anticipated emission levels. In general, they have performed quite satisfactorily and received wide endorsement from plant operators and maintenance personnel.

Our survey of these installations shows that the most typical problems are high pressure drop and bag failure caused by condensation and fine particulate, abrasion from coke breeze, corrosion brought on by high moisture and the general atmosphere of the coke battery, and reduced performance caused by improper equipment design. Attention to each of these areas is necessary in designing or improving these collection systems.

The work described in this paper was not funded by the U. S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

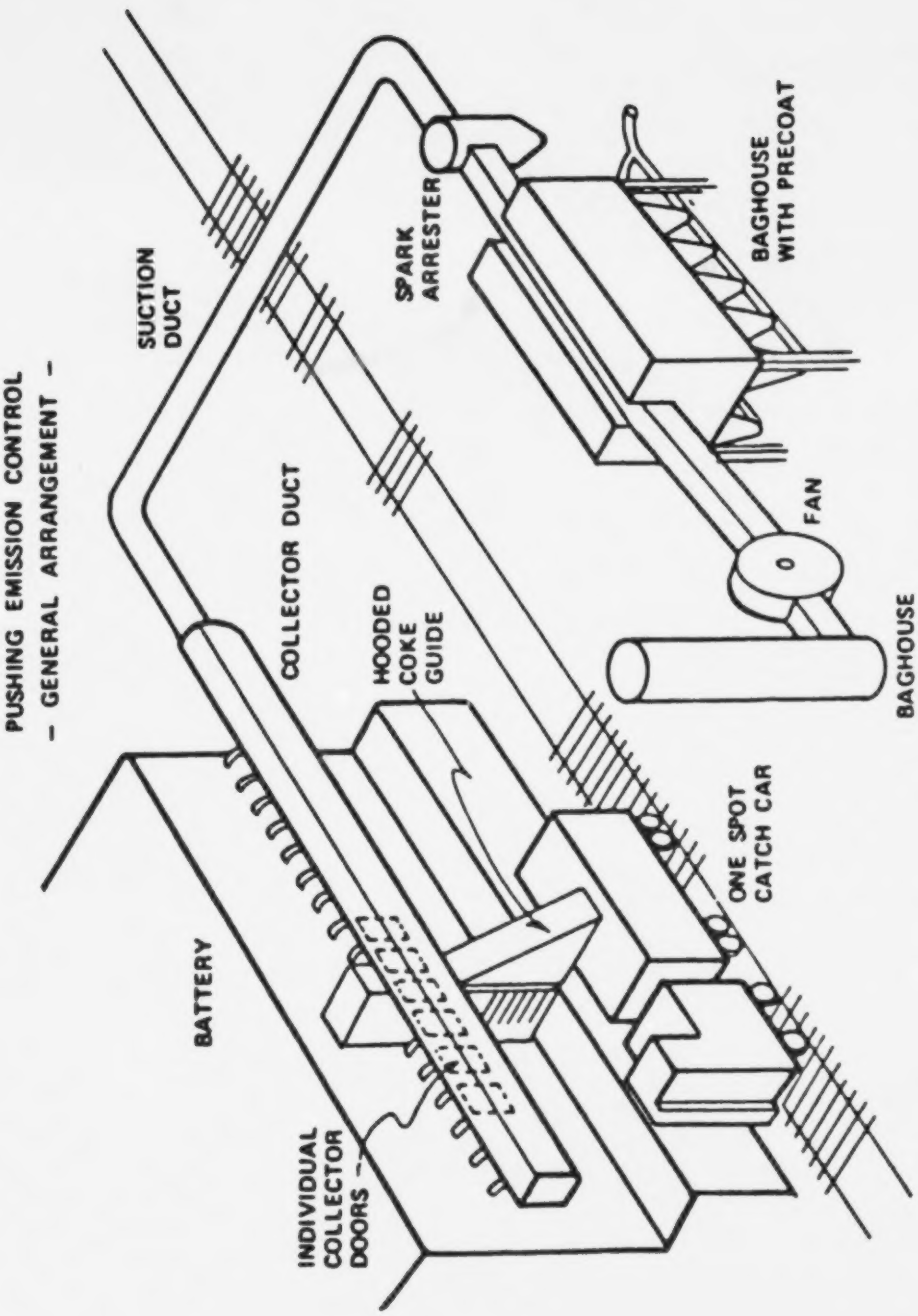

PUSHING EMISSION CONTROL
– GENERAL ARRANGEMENT –
SUCTION DUCT
SPARK ARRESTER
BAGHOUSE WITH PRECOAT
COLLECTOR DUCT
FAN
HOODED COKE GUIDE
BAGHOUSE STACK
BATTERY
ONE SPOT CATCH CAR
INDIVIDUAL COLLECTOR DOORS

Figure 1

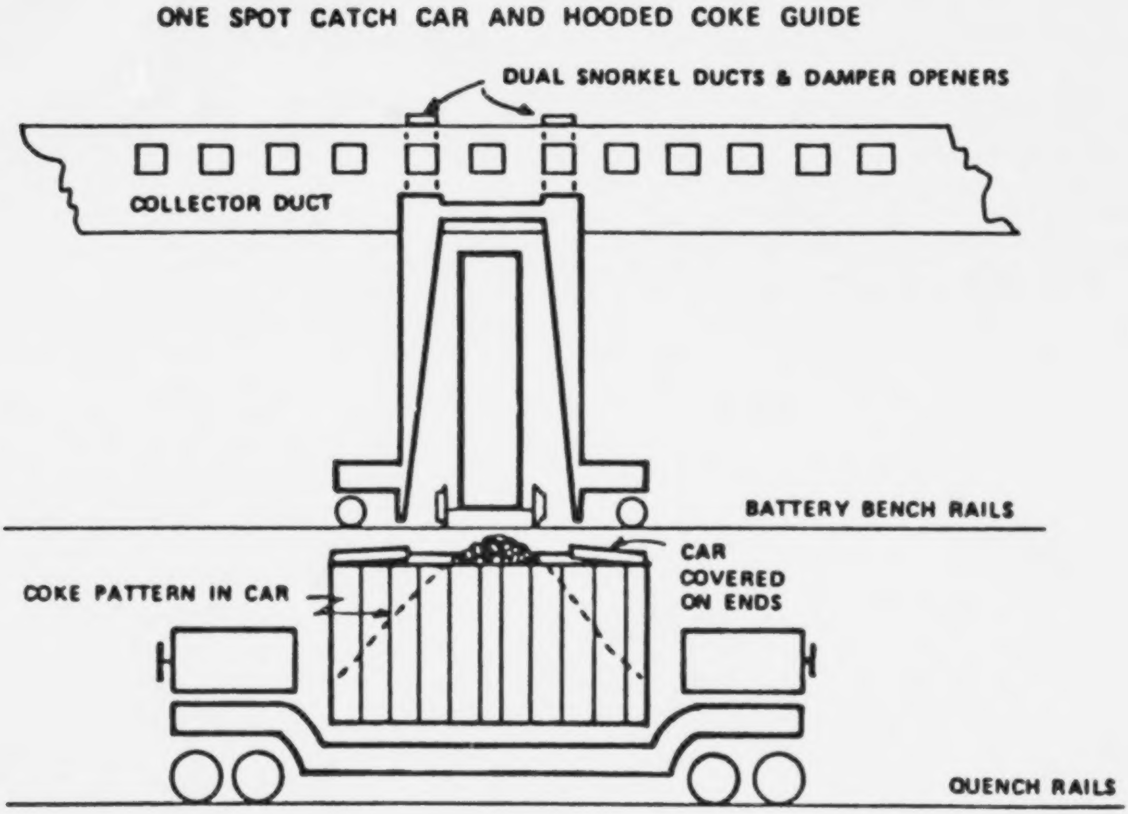
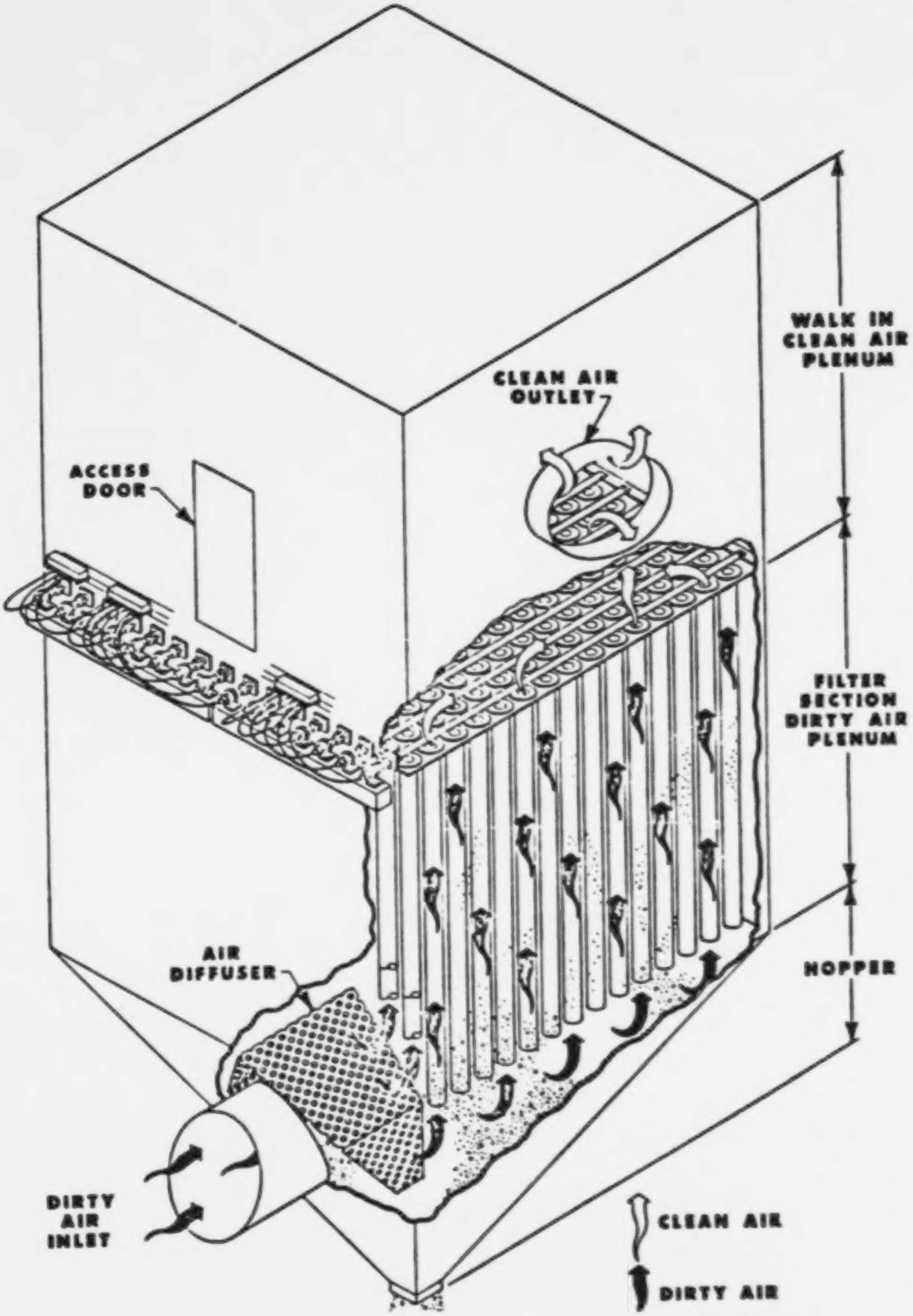

ONE SPOT CATCH CAR AND HOODED COKE GUIDE
DUAL SNORKEL DUCTS & DAMPER OPENERS
COLLECTOR DUCT
BATTERY BENCH RAILS
CAR
COVERED
ON ENDS
COKE PATTERN IN CAR
QUENCH RAILS

Figure 2


WALK IN CLEAN AIR PLENUM
CLEAN AIR OUTLET
ACCESS DOOR
FILTER SECTION DIRTY AIR PLENUM
AIR DIFFUSER
HOPPER
DIRTY AIR INLET
CLEAN AIR
DIRTY AIR

PULSE JET COLLECTOR

Figure 3

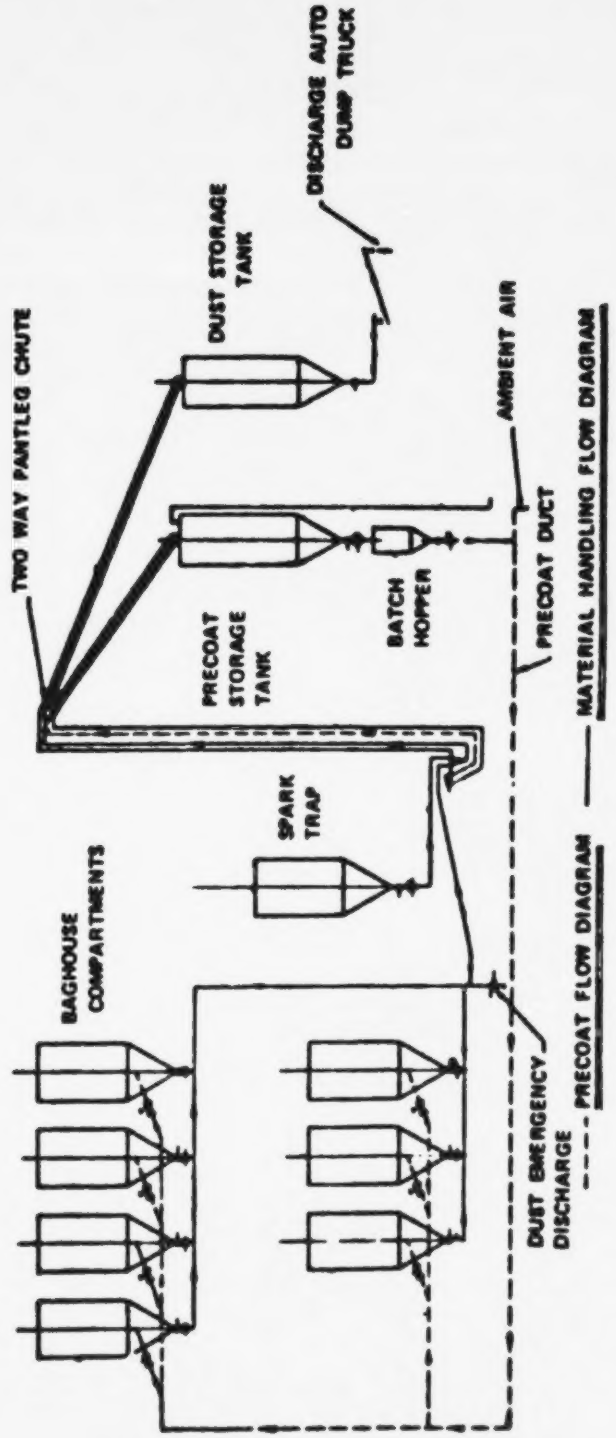

BAGHOUSE COMPARTMENTS
DUST EMERGENCY DISCHARGE
SPARK TRAP
PRECOAT STORAGE TANK
BATCH HOPPER
PRECOAT DUCT
TWO WAY PANTLEG CHUTE
AMBIENT AIR
DUST STORAGE TANK
DISCHARGE AUTO DUMP TRUCK
– – – PRECOAT FLOW DIAGRAM
—— MATERIAL HANDLING FLOW DIAGRAM

Figure 4

EXHIBIT I

Coke Pushing Emission Control Questionnaire

Size of Battery: ____________________

Number of Ovens: ____________________

Type of Collecting Hood: e.g., Shed, Traveling Hood/Minister Stein, Single Spot/Mitsubushi ____________________

Design Gas Volume & Temperature: ACFM & $^{\circ}$F ____________________

Type of Control System & Years of Operation:
    Wet Scrubber ____________________
    Shaker Fabric Filter ____________________
    Reverse Air Fabric Filter ____________________
    High Ratio Pulse Fabric Filter ____________________
    Other (   ) ____________________

For Fabric Filter:
    Design Air/Cloth Ratio (Net & Gross) ____________________
    Design Pressure Drop ____________________
    Bag Type: e.g. Nomex,Dacron,Glass ____________________

For Pulse FF: Is Cleaning Done "On" or "Off-Line"? ____________________

Precoat System: Continuous (In Inlet Plenum), Intermittent (Directly in Each Compartment), None ____________________

Precoat Material: e.g., Limestone, Flyash Etc. ____________________

Operating Experience

How Well Are Pushing Emissions Ventilated ____________________

Pressure Drop Across Bags/Scrubber ____________________

Operating Air/Cloth Ratio (Net & Gross) ____________________

Baglife, Months ____________________

Precoat Material Usage ____________________

Corrosion Problem Areas ____________________

Reason for Bag Failure (If Any) ____________________

Reason for Reduced Performance (If Any) ____________________

Any Action Leading to Improved Operation ____________________

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APPLICATION OF THE ELECTROSCRUBBER FILTER TO ISCOR'S ALKALI-CONTROLLED IRON ORE SINTERING PLANTS

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1.0 ABSTRACT

It has been known for quite some time that alkalis in the blast furnace are contributors to a wide range of operational problems. ISCOR has found, however, that when a calcium chloride impregnated sintermix is ignited on the sinter bed, the result is that the temperature is found to be sufficiently high to cause the calcium chloride in the mixture to react with the potassium in the ore and form potassium chloride, which is exhausted with the waste gases from the bed as a white fume. The resultant sinter is low in alkali and proves most suited to proper blast furnace operation.

A problem develops in particulate collection from the sinter machine, however, because the potassium chloride fume is extremely fine (up to 85% < 1 micron) and the gases include SO_2, SO_3, fluorides, and hydrochloric acids. ISCOR evaluated particulate collection technology and conducted some testing to determine the suitability of dry electrostatic precipitators, high energy wet scrubbers, fabric filters, and static bed granular filters of the type used on sintering processes in Weirton, West Virginia and Duisburg, Germany. For various reasons, ISCOR deemed these choices as

inappropriate. However, successful pilot tests using the ELECTROSCRUBBER* Filter, an electrostatically enhanced moving bed granular filter that has been applied to over 14,000,000 m^3/hr (8,000,000 ACFM) of gas from industrial processes, including one other sinter machine, led ISCOR to the conclusion that this filter would be able to meet stack emissions requirements of 110 mg/Nm^3 (0.025 gr/ACF).

This paper describes the theory of operation of the ELECTROSCRUBBER Filter, the pilot model tests, the filter design criteria, and the two installations at Vanderbijlpark and Newcastle, South Africa. Emphasis is placed on performance, operation, and maintenance data of the ELECTROSCRUBBER Filters since startup. The two projects - 1,500,000 m^3/hr (875,000 ACFM) for Newcastle and 1,470,000 m^3/hr (865,000 ACFM) for Vanderbijlpark - started up in early 1983. Success of these two very large systems, as evidenced by compliance level emissions performance on the submicron particulate, will demonstrate that the relatively new ELECTROSCRUBBER Filter technology is applicable to the alkali-controlled sintering process. It will also provide the steel industry with experience valuable to particulate collection on other steel making processes as well.

2.0 THE PROBLEM WITH ALKALIS IN THE BLAST FURNACE

Blast furnace performance in South Africa has long been plagued by high pressure and unstable operating conditions giving rise to fluctuating slag chemistry and iron composition. High coke rates and low iron production were blamed on the coke quality which placed a restraint on furnace size.

Research published by Stelco in 1973 (1), and by the British Steel Corporation in 1978 (2), has shown that alkalis in the blase furnace burden are responsible for most operating problems experienced. This was also the case in South Africa, where the K_2O input was 5.5 kg per ton hot metal. Prior to the introduction of external desulfurization, high slag basicity practice was used to remove sulfur. This aided accumulation of recirculating alkali loads resulting at times in catastrophic slips and chilled hearths.

Two solutions were indicated for alkali control:

(a) To ensure that no alkali buildups would occur by balancing the alkali input and output by slag basicity control.

(b) To restrict input by limiting alkali in the raw materials.

The first approach became possible with external hot metal desulfurization facilities which have allowed the reduction of slag basicity $(CaO + MgO)/SiO_2$ from 1.4 to 1.15 resulting in hot metal sulfurs increasing from 0.03% up to 0.15%.

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*Registered U.S. Patent and Trademark Office

The second approach was the more difficult but was achieved by addition of $CaCl_2$ to the Sinter raw material mix. Alkali levels could be reduced from 0.29% K_2O to 0.08% by the addition of 2.6 kg $CaCl_2$/ton sinter. (3)

Since implementation of these solutions blast furnace operation has improved as expected. However, concentration of potassium and sodium chlorides in the windbox exhaust gases rose to unacceptable levels, and the air pollution control devices were unable to handle this material. The Air Pollution Control Authority required a maximum emission level of 0.11 gram/Nm^3, (0.025 gr/ACF) in this instance, and was only prepared to permit limited testing on the existing devices.

3.0 SEARCH FOR SUITABLE PARTICULATE COLLECTOR

3.1 TESTS ON EXISTING DUST COLLECTION DEVICES

At Vanderbijlpark sinter plant, which emitted 0.2 grams/Nm^3 (0.048 gr/SCF) during normal operation, the emission rose to 1.5 gram/Nm^3 (0.62 gr/SCF) when sintering with calcium chloride addition. It was not possible to improve the collection efficiency of the cyclones.

Various attempts were made to improve the performance of the Newcastle Electrostatic Precipitators, also without success. It was concluded that the high resistivity of the potassium chloride and the fineness of the particles were insurmountable obstacles to satisfactory precipitator performance. The chemical analysis and size distribution of the particles are shown in Tables 3.1 and 3.2.

3.2 CONSIDERATION OF CURRENTLY AVAILABLE METHODS

Experiments were also performed using a 5% side stream of the gas flow at Vanderbijlpark. A venturi scrubber with 200 mm (8 in.) throat dia. was tested at various gas and water flowrates using pressure differentials up to 10 kPa (1.47 psi.). Collection efficiencies of 90% were obtained under best conditions, but the energy required and rapid buildup of dissolved solids and acidity in the liquor were unacceptable, as the dust collected was 95% water soluble.

Corrosion prevention measures and effluent disposal problems would further increase the cost of equipment, and the recovery of the potassium chloride, which is an imported mineral, would have required additional plant and energy input.

Wet electrostatic precipitation was also considered. The fan energy required would have been acceptable, but the water system problems would have been similar to those experienced with venturi scrubbing. ISCOR preferred a dry collection option, for recovery of the dust, as conservation of water resources is of prime importance and will become increasingly so.

Baghouse filtration was also considered, but for practical reasons such as high acid dewpoint and the presence of fluorides and

TABLE 3.1 CHEMICAL ANALYSIS OF DUST FROM STACK SAMPLES

	NEWCASTLE FEB. 1979	VANDERBIJLPARK SEPT. 1979
Potassium	42.5%	37.1
Sodium	1.99%	4.9
Chloride	46.5	44.6
Calcium	0.26%	0.91
Lead	0.16%	0.26
Sulphate	nd	1.21
Zinc	nd	0.02
Alumina	nd	0.25
Magnesium	nd	0.24
Haematite	nd	5.8
Silica	nd	0.62
Water insolubles%	1.6%	6.5%

TABLE 3.2 SINTER PLANT WASTE GAS STACK PARTICLE SIZE DISTRIBUTION - NEWCASTLE

SIZE INTERVAL MICRONS	0 - 0.2	0.2 - 0.3	0.3 - 0.8	0.8 - 1.7	1.7 - 3.0
% MASS	1.76	14.4	39.4	44.5	0

DATE: FEB. 1979

METHOD: MICROSCOPE COUNT OF CELLULOSE MEMBRANE FILTER SAMPLE hydrochloricacid in the flue gas, was rejected as high maintenance cost for bag replacement was feared. Gravel filtration was considered to be less affected by such adverse conditions.

Gravel filtration had been developed in Europe (by M. and W. Berz in 1957) for application to high temperature dust collection on cement clinker plants. The limitationsof their system were soon apparent. A further development was the "Drallschicht" filter which consisted of a 2-3 mm dia., 90-100 mm thick gravel layer on a horizontal screen which was air cleaned in upflow mode, while raked mechanically. Such filters were constructed in modules of 11.4 m^2 each. By 1977 a total gas volume of 33 x 10^6 m^3h^{-1} was being treated worldwide in such units. A typical application is the 3000 tpd. clinker cooler at Onoda Cement Works in Japan, which treats 700,000 m^3h^{-1} in such units.

A gravel bed filter system funded by the E.P.A., using similar modules, has also been constructed, operated and evaluated at the National Steel Weirton Division, No. 2 Sinter Machine (contract No. 68-02-1862). Tests with garnet and steel grit media resulted in collection efficiencies better than 90% for dust under normal sintering conditions. Problems were experienced, however, with condensation of moisture and accretion of lime and dust on the media, so that extensive plant modifications and additional controls were required.

3.3 TEST WITH GRAVEL FILTERS ON ALKALI FUMES

Permission was granted by the air pollution control authority for limited operation of the sinter plant in the de-alkalizing mode for test purposes, during favorable atmospheric conditions.

A test plant consisting of two Lurgi CS - filter modules each of 11.4m^2 (114 sq.ft.) filtering area was set up to filter a side stream, withdrawn from the sinter windbox extraction fan exhaust duct. The tests were performed by a team of Lurgi and Iscor staff. Results under normal sintering conditions were excellent. However under de-alkalizing conditions some interesting operating deviations were encountered.

1. The filters were able to capture the fumes of 0.45 micron median particle diameter at efficiencies up to 81%, using 200 mm deep gravel bed of 1.7 - 2.0 mm media.

2. Pressure differential increased very rapidly due to the buildup of a snowlike deposit on the gravel layer. This was removed completely during backflush cycles, which had to be more frequent, however, to maintain gravel bed pressure differential within acceptable limits.

3. The collected dust, removed in a cyclone, had a bulk density of 0.11 gram/Nm^3 and was 95% water soluble. It consisted mainly of potassium chloride: see Table 3.1.

4. Using coarser gravel of 2.2 mm dia. with 120 mm (5 in.) bed depth, the pressure drop and short filtration cycles were still unacceptable.

5. The bulk volume of the dust collected during the de-alkalizing sintering mode was 35 times greater than that collected as during normal sintering.

At this point it was concluded that this application was not quite suited for the C.S. Filter. A chance contact with Combustion Power Company (CPC) was followed up, and after obtaining information about CPC's granular filter, it was decided that this technology would be investigated. The CPC filter is different from the Lurgi filter in that it utilizes a continuously cleaning, moving bed of gravel. Although CPC had an older model system in operation on a sinter plant at Great Lakes Steel, Detroit, Michigan, the present version, the ELECTROSCRUBBER Filter (ESF), incorporates an electrostatic enhancement feature that held promise for capturing the fine alkali fume. See Appendix A for a detailed discussion of the principle of operation of the ESF.

A logistic problem developed however with regard to the capability of CPC's sending of their field pilot test unit to South Africa from the United States within the project's time and economic constraints. But, since CPC had a larger, 7000 ACFM test unit on its premises, it was decided to perform the tests there. The use of resuspended dust in the test unit, e.g., using the dust collected from the Lurgi gravel bed test unit, was not considered feasible because the nature of the particles would change during shipment. And, of course, the very fine particles which were not captured during the in-situ Lurgi test would not be present at all, even if a sound method of dust resuspension were found.

A method was sought, therefore, where sinter plant emissions could be remotely approximated. It was concluded that the real problem was the KCl and that a successful test at CPC would be one that demonstrated high efficiency on volatized KCl. After considering several alternatives, it was decided that a specially constructed burner could be installed ahead of their test unit to produce the fume. The construction of the "fume generator" included a natural gas burner, a series of refractory brick checkers, and a pumping system whereby a saturated solution of KCl salt in water could be sprayed onto the hot bricks. See Figure 3.1 for a process schematic of the fume generator/ELECTROSCRUBBER Filter Test Unit.

After correcting some problems with control of the fume generator, the tests proceeded. It was apparent that the generator produced a very good approximation of the actual sinter plant emissions: 90% of the dust produced was in the submicron range, the average dust loading was 0.26 gr/ACF, and the temperature was about 300°F. The gas flow into the ELECTROSCRUBBER Filter was adjusted to simulate the internal gas velocities as would be seen in a full sized unit.

Particulate sampling data is shown in Table 3.1. Opacity and electrostatic grid current draw are shown in Table 3.4. Much effort was expended during the test in securing accurate data on the filter's fractional

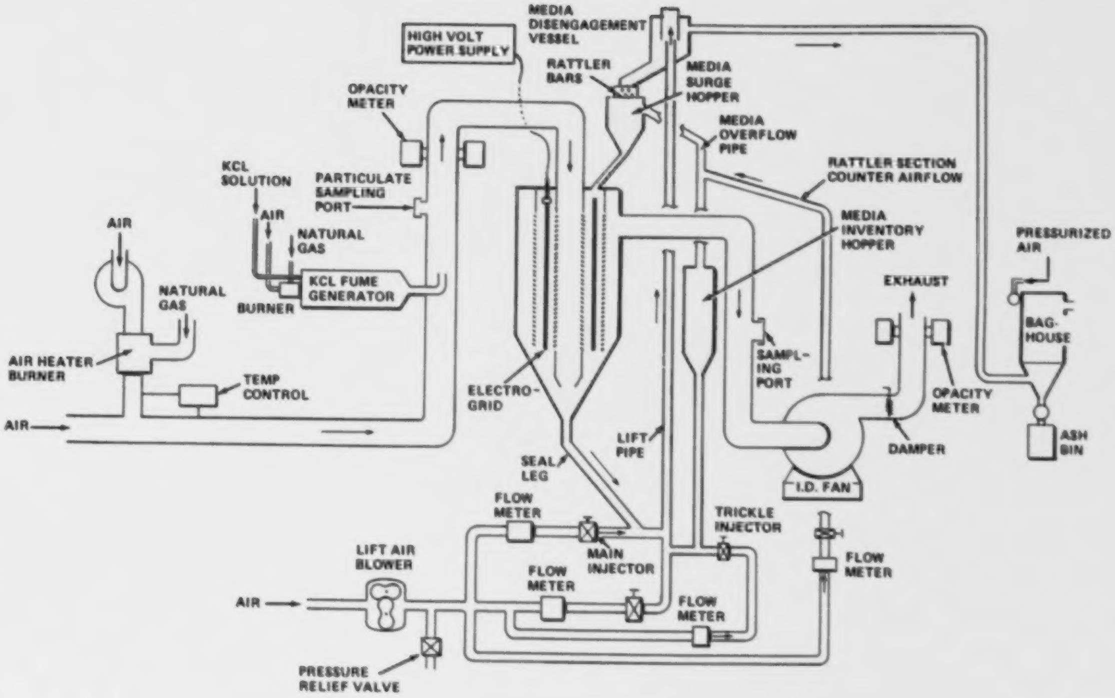

MEDIA DISENGAGEMENT VESSEL
HIGH VOLT POWER SUPPLY
RATTLER BARS
MEDIA SURGE HOPPER
OPACITY METER
MEDIA OVERFLOW PIPE
RATTLER SECTION COUNTER AIRFLOW
KCL SOLUTION
PARTICULATE SAMPLING PORT
AIR
NATURAL GAS
MEDIA INVENTORY HOPPER
PRESSURIZED AIR
AIR
EXHAUST
NATURAL GAS
KCL FUME GENERATOR
BURNER
BAG-HOUSE
AIR HEATER BURNER
TEMP CONTROL
SAMPL-ING PORT
OPACITY METER
ELECTRO-GRID
AIR
LIFT PIPE
DAMPER
ASH BIN
SEAL LEG
I.D. FAN
FLOW METER
TRICKLE INJECTOR
LIFT AIR BLOWER
MAIN INJECTOR
FLOW METER
FLOW METER
AIR
FLOW METER
PRESSURE RELIEF VALVE
FLOW METER

Figure 3.1 Schematic of 7000 ACFM ELECTROSCRUBBER Filter Pilot Test Unit

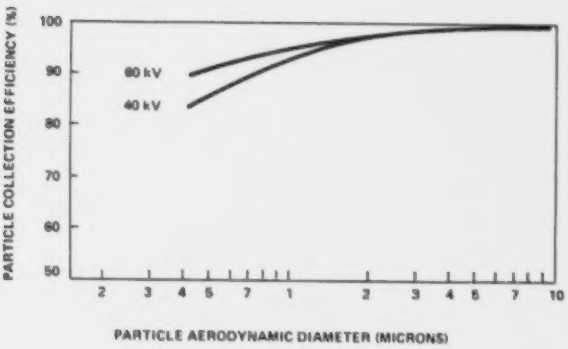


Figure 3.2 ELECTROSCRUBBER Filter Pilot Test: Fractional Particulate Collection vs. Electrostatic Grid Voltage

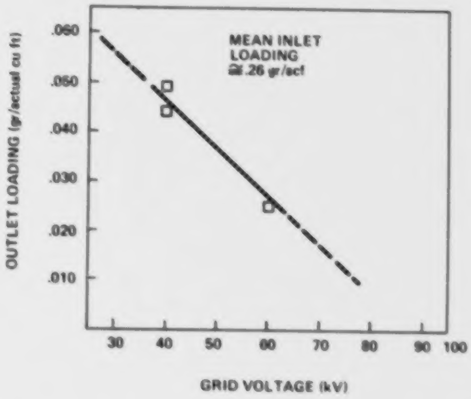


Figure 3.3 ELECTROSCRUBBER Filter Pilot Test: Outlet Loading vs. Electrostatic Grid Voltage

TABLE 3.3 ELECTROSCRUBBER FILTER PILOT TEST: DATA SUMMARY

TEST NO.	TEST DATE	INLET GASFLOW (ACFM)	GAS TEMPERATURE (°F) INLET	GAS TEMPERATURE (°F) OUTLET	MEDIA RATE (LB/MIN)	GRID VOLTAGE (KV)	OPACITY % INLET(3)	OPACITY % OUTLET(4)	OPACITY % OUTLET(5)	LOADINGS (Gr/ACF) INLET	LOADINGS (Gr/ACF) OUTLET	EFF (%)
SA-CO	4-24-80	5000	297	170	150	60	80	60	20	.26(2)	.025	91.2
"	"	4800	291	200	150	60	80	60	20	.30(1)(7)	.037	--
SA- 9	4-25-80	4800	292	185	150	40	79	73	26	.29(2)	.044	88.7
"	"	4700	293	200	150	40	65	55	17	.25(1)	.052	82.8
SA-9R	5- 2-80	4800	300	209	150	40	74	68	24	.22(2)	.049	81.8
"	"	4800	298	214	150	40	72	65	22	.25(1)	.050	83.3
SA-10	4-25-80	4800	290	199	300	60	63-30	49-20	--	.24(2)(6)	.025	--
"	"	4800	293	196	300	60	69	53	16	.23(1)	.045(8)	--
SA-10R	"	4700	295	199	300	60	78	59	19	.29(2)	.013(7)	--
SA-11	"	4600	285	200	150	60	77	60	20	.26(2)	.029	90.0
"	"	4900	299	200	150	60	76	58	19	.28(1)	.010(7)	--

1) Andersen Impactor Sample
2) EPA-5 Sample
3) Double-Pass opacity in 18" diameter duct
4) Double-Pass opacity - 76" diagonal pass through a 18" diameter duct
5) Double-Pass opacity - 18" duct calculated from outlet opacity-Note #4
6) Sample questionable due to fume generator malfunction
7) Sample invalid due to sampling error
8) Sample invalid due to contamination of sample

TABLE 3.4 ELECTROSCRUBBER FILTER PILOT TEST:
OUTLET OPACITY VS. ELECTROSTATIC GRID VOLTAGE

	TEST SA-9 INLET OPACITY=78%(1)		TEST SA-11 INLET OPACITY=71%(1)		TEST SA-10R INLET OPACITY=71%(1)		TEST SA-9R INLET OPACITY=73%(1)	
GRID VOLTAGE (KV)	Grid Amperage (MA)	Outlet Opacity (%) (2)	Grid Amperage (MA)	Outlet Opacity (%) (2)	Grid Amperage (MA)	Outlet Opacity (%) (2)	Grid Amperage (MA)	Outlet Opacity (%) (2)
0	0	92	0	88	0	94	0	93
10	--	--	--	--	0	90	0	84
20	0	84	0	76	0	93	0	76
30	0	70	0	67	0	75	0.1	68
40	0	62	0	60	0.1	66	0.2	63
50	0	61	0	53	0.1	60	0.2	53
60	0	55	0	49	0.2	57	0.3	48
70	0.2	51	0.3	45	0.3	51	0.4	48
75	0.4	49	0.3	43	0.3	47	0.5	47

(1) Double-Pass Opacity - 18" Duct

(2) Double-Pass Opacity - 76" Diagonal Pass Through a 18" Duct.

efficiency. See Figure 3.2. For outlet loading vs. grid voltage, see Figure 3.3. These results clearly showed that the ELECTROSCRUBBER Filter was capable of producing the desired performance. (A detailed analysis did indicate that the full sized units would need to operate at electrostatic grid voltages of at least 75KV in order to produce required performance.) Physical observations during the test, e.g., filter pressure drop, normalcy of media recirculation, evidence of louver pluggage, etc., were all positive. Note expected, but very low performance, of the filter with no electrostatic grid voltage. An interesting observation can be made regarding the power consumption with the electrostatic grid energized. The data on Table 3.4 indicates that at 75KV and 5000 ACFM, the current drain was 0.5 ma maximum. This equilibrates to 7.5 watts per 1000 ACFM. Newcastle's 875,000 ACFM, if fitted with ELECTROSCRUBBER Filters, would require less than 7000 watts of power to produce the desired performance.

The results from gravel filter tests were sufficiently promising that it was decided to add gravel filtration plants at both Vanderbijlpark and Newcastle sinter plants to the outlet side of existing gas cleaning equipment.

4.0 PROJECT DESCRIPTIONS

At Vanderbijlpark sinter plant, it was decided to add 8 Model ES1000 units (see Figure 4.1) behind the existing primary cyclones. Booster fans were added, and the exhaust gas emitted through a new 100 m (328 ft.) stack. For the Newcastle sinter plant it was decided to retain the electrostatic precipitator and install the 8 ES1000 units between the ESP outlet and the existing stack (see Figure 4.2). A schematic drawing of 1 ES1000 is shown in Figure 4.3.

The specifications (outlined in Table 4.1) and process schematics (outlined in Figures 4.4 and 4.5) are almost identical except for minor details.

5.0 OPERATION SINCE START UP

5.1 MECHANICAL PROBLEMS

High Voltage Problems - The pilot tests at CPC determined that at maximum inlet loading of 0.361 gr/acf (1 500 mg/Nm^3) (Vanderbijlpark), a voltage of 75KV was required to provide for a performance of 0.0261 gr/acf. A 100KV transformer was therefore selected. The larger media now in use because of process pressure drop problems (see below) underscores the need for the capability of attaining at least 75KV because, all other things equal, the larger the media, the poorer the performance.

It seems, however, that, although the transformer is capable of 100KV output, that the high voltage insulator supporting the electrostatic grid and the high voltage cables can withstand only 60KV. CPC is considering

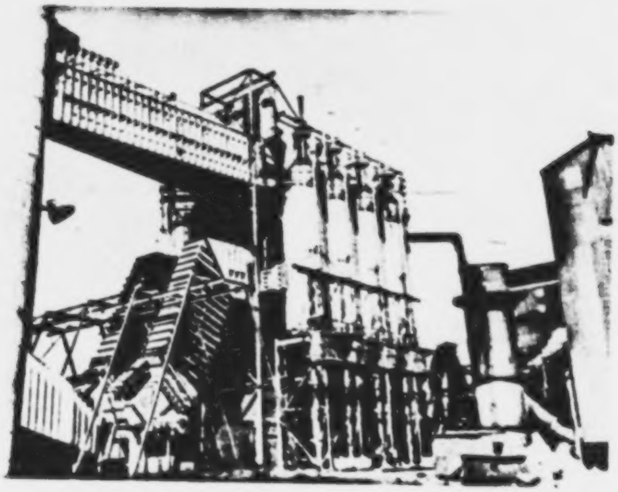


Figure 4.1 Photo of Vanderbijlpark's 8 ES1000's

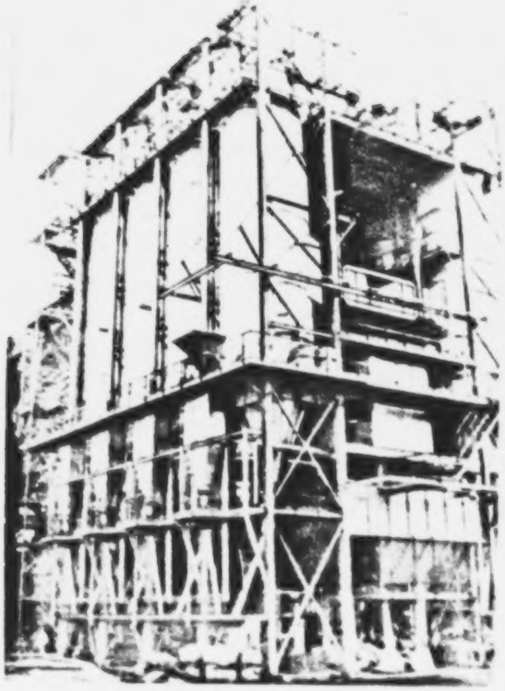


Figure 4.2 Photo of Newcastle's 8 ES1000's

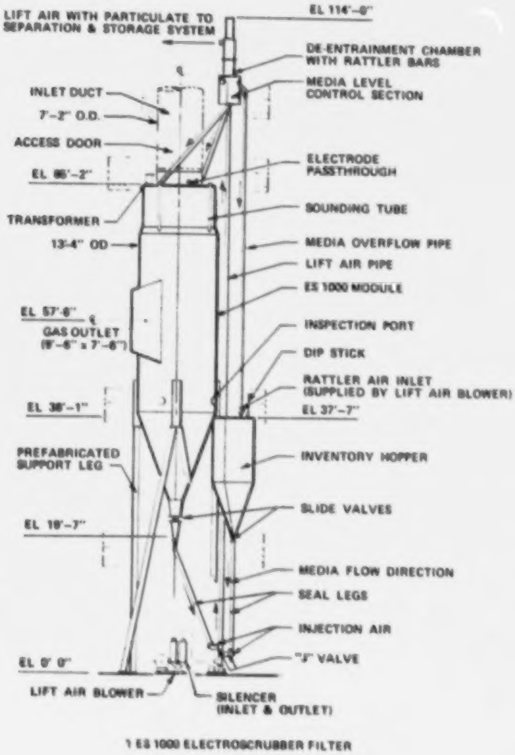

LIFT AIR WITH PARTICULATE TO SEPARATION & STORAGE SYSTEM
EL 114'-0"
DE-ENTRAINMENT CHAMBER WITH RATTLER BARS
MEDIA LEVEL CONTROL SECTION
INLET DUCT
7'-2" O.D.
ACCESS DOOR
EL 86'-2"
ELECTRODE PASSTHROUGH
TRANSFORMER
SOUNDING TUBE
13'-4" OD
MEDIA OVERFLOW PIPE
LIFT AIR PIPE
ES 1000 MODULE
EL 57'-6"
GAS OUTLET (9'-6" x 7'-6")
INSPECTION PORT
DIP STICK
RATTLER AIR INLET (SUPPLIED BY LIFT AIR BLOWER)
EL 38'-1"
EL 37'-7"
PREFABRICATED SUPPORT LEG
INVENTORY HOPPER
SLIDE VALVES
EL 19'-7"
MEDIA FLOW DIRECTION
SEAL LEGS
INJECTION AIR
"J" VALVE
EL 0' 0"
LIFT AIR BLOWER
SILENCER (INLET & OUTLET)
1 ES 1000 ELECTROSCRUBBER FILTER

Figure 4.3 Schematic of 1 ES1000 ELECTROSCRUBBER Filter

TABLE 4.1 ELECTROSCRUBBER FILTER SPECIFICATIONS
ISCOR'S CONTINUOUS IRON ORE SINTERING PLANTS

		VANDERBIJLPARK	NEWCASTLE
EQUIPMENT		EIGHT (8) MODEL ES1000	EIGHT (8) MODEL ES1000
	Media Recirculation System:	One (1), 6" per each ES1000 module	One (1), 6" per each ES1000 module
	Transformer:	8 @ 100 kV, 125 ma = 157 kVA connected, 100 kVA operating	8 @ 100 kv, 125 ma = 157 kVA connected, 100 kVA operating
	Lift Blower HP:	8 @ 50 hp = 400 hp connected, 300 hp operating	8 @ 50 hp = 400 hp connected, 300 hp operating
	Floor Space:	6 @ 14' x 14' = 1568 sq ft total	6 @ 14 ft x 14 ft = 1568 ft^2 total
	Gas Flow Direction:	Inside-to-outside, separate stack	Inside-to-outside, separate stack
	Operating Pressure:	Negative	Negative
PRECLEANER		SINGLE-STAGE CYCLONES	ELECTROSTATIC PRECIPITATOR
INLET CONDITIONS SPECIFIED			
	Gas Flow:	865,000 acfm (1,470,000 m^3/HR)	875,000 acfm (1,500,000 m^4/HR)
	Gas Temperature:	302 F (150 C)	374 F (190 C)
	Gas Moisture:	1.6% (weight)	2.6 - 3.9% (weight)
	Dust:	Primarily Potassium Chloride	Primarily Potassium Chloride
	Inlet Loading:	0.361 gr/acf (1,500 mg/Nm^3)	0.276 gr/acf (1,200 mg/Nm^3)
	Particle Size Distribution:	Less than 1 micron - 72.7% 1 to 2 microns - 13.2% 2 to 5 microns - 14.1% Greater than 5 microns - 0	ESP OFF ESP ON Less than 0.2 microns 50% 34% 0.2-0.5 microns 23% 30% 0.5-1.0 microns 13% 19% 1.0-2 microns 8% 11% 2-7 microns 5% 5% Greater than 7 microns 1% 1%
DUTY CYCLE		CONTINUOUS	CONTINUOUS
REQUIRED OUTLET CONDITIONS			
	Loading:	0.0261 gr/acf (110 mg/Nm^3)	0.025 gr/acf (110 mg/Nm^3)
	Opacity	Not specified	Not specified

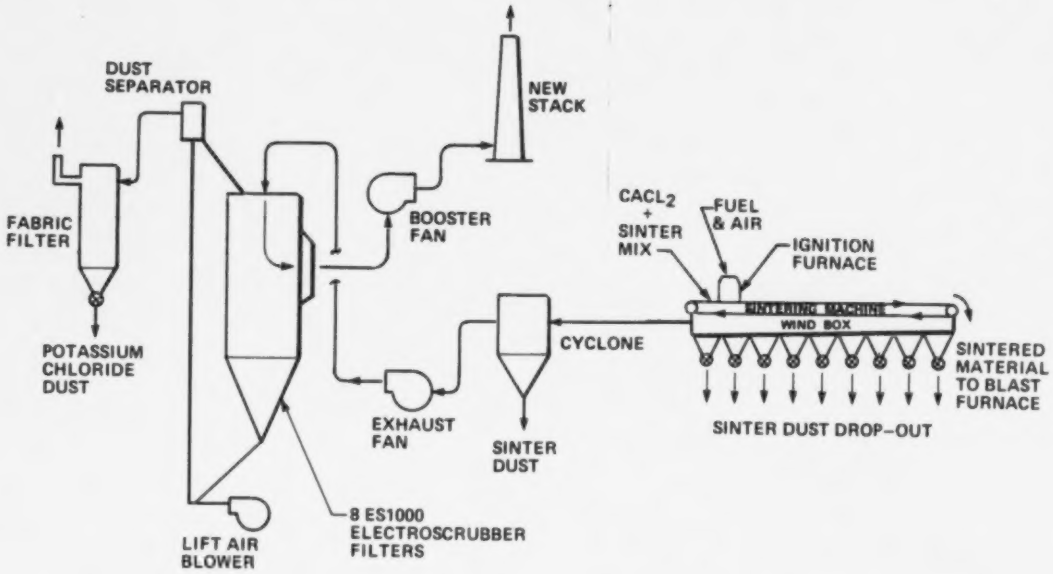

DUST SEPARATOR
NEW STACK
FABRIC FILTER
BOOSTER FAN
CACL2 + SINTER MIX
FUEL & AIR
IGNITION FURNACE
SINTERING MACHINE
WIND BOX
CYCLONE
POTASSIUM CHLORIDE DUST
SINTERED MATERIAL TO BLAST FURNACE
EXHAUST FAN
SINTER DUST DROP-OUT
SINTER DUST
8 ES1000 ELECTROSCRUBBER FILTERS
LIFT AIR BLOWER

Figure 4.4 8 ES1000 ELECTROSCRUBBER Filters on ISCOR's Continuous Iron Ore Sintering Plant Vanderbijlpark , South Africa

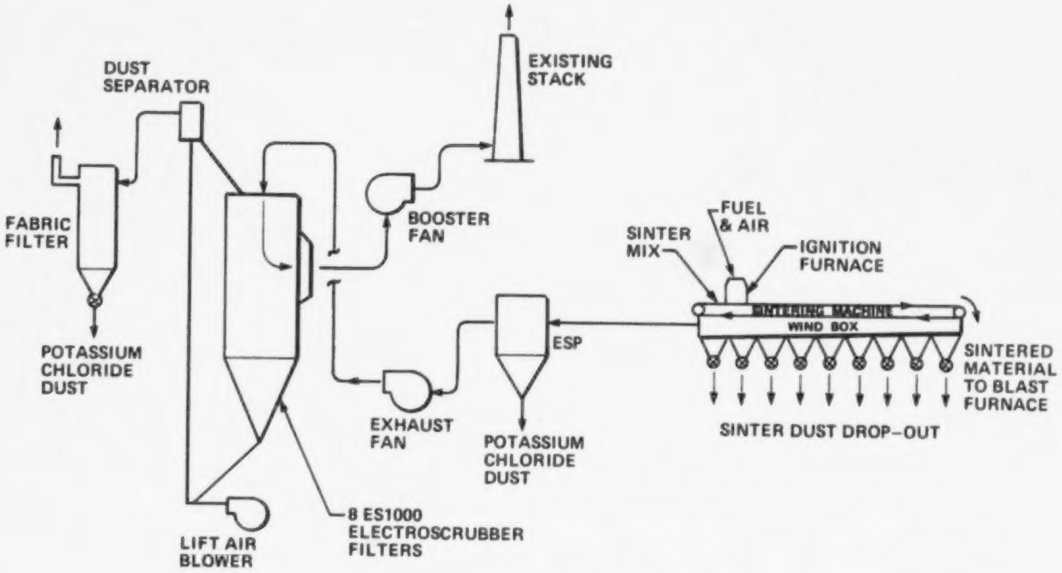

DUST SEPARATOR
EXISTING STACK
FABRIC FILTER
BOOSTER FAN
FUEL & AIR
SINTER MIX
IGNITION FURNACE
SINTERING MACHINE
WIND BOX
ESP
POTASSIUM CHLORIDE DUST
SINTERED MATERIAL TO BLAST FURNACE
EXHAUST FAN
SINTER DUST DROP-OUT
POTASSIUM CHLORIDE DUST
8 ES1000 ELECTROSCRUBBER FILTERS
LIFT AIR BLOWER

Figure 4.5 8 ES1000 ELECTROSCRUBBER Filters on ISCOR's Continuous Iron Ore Sintering Plant Newcastle, South Africa the design of an improved insulator and has suggested a high voltage cable of higher rating.

Material Wear - The media return tubes and DEV have been reported as wearing faster than expected. CPC indicates that, with several years of operational experience on systems with similar designs, that there are areas in the pneumatic system in need of a more conservative design approach. Abrasion-resistant materials have been suggested for some areas; larger diameter pipes (to slow down the media velocity at a given massflow rate) have been suggested for other areas. Also, a more detailed procedure for "Tuning" the air and media flows is being developed which should also assist in component longevity. Recent measurements indicate that media attrition rates have been at a very low rate of 0.3 tons per module per week, or less than 10% per year. This is a positive indication that material wear will be within allowable expectations.

5.2 PROCESS PROBLEMS

Primary Process Problems - Without question, the biggest problem experienced has been the interaction of the particulate with the media. During the simulation tests at CPC with the KCl fume generator, no problems related to particulate buildup, media flow irregularities, high pressure drop, etc. were encountered. Upon startup of the full size units on the actual process, however, it was apparent that something was different. The pressure drop immediately climbed past the capability of the I.D. fan. Part of the problem was due to too small media obtained from the supplier in the United States. Most of the problem, however, was traced to the nature of the process itself. The dust, actually composed of mostly KCl, appears to be captured on the first few layers of media, rather than through the thickness of the media bed. This dust concentration "artificially" raises the pressure drop.

To accommodate the problem, larger, local media (6.6+ mm vs. design 4.8 mm) was introduced into the units, reducing the pressure drop to a manageable 190 mm (9-10. IWG). Although there were performance concerns because of the large media, there was really no other choice, other than reduction or elimination of the $CaCl_2$ addition rate to the mix. Regarding the local vs. U.S. media, it was fortunate that the material had been under evaluation already for possible later use in the modules. It has been found to be, for the most part, suitable. (See media attrition comments above.)

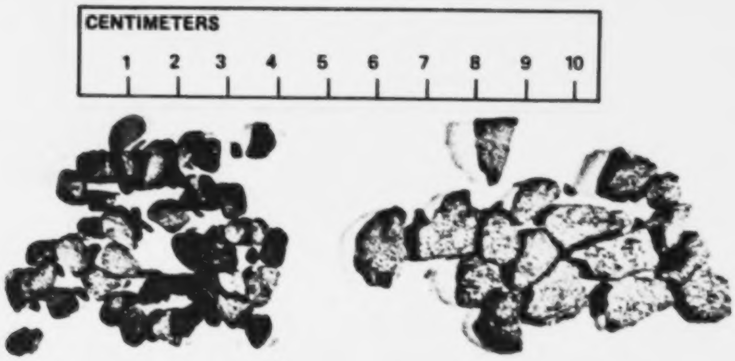
Secondary Process Problems - Notwithstanding the larger media, the dust/media mixture exhibited flow irregularities in the media cavities. ("Channeling" is caused by dust buildups on the cone.) These irregularities in turn probably contributed to observations of media in the outlet duct. (The process gas will tend more to pass through the moving-media areas than through the stopped areas, causing high gas velocities which entrain the media that naturally falls through the louvers.) The irregular media flow was quite possibly the cause as well of bent electrostatic grid cages and (resulting) poor performance.

The flow irregularities problem was first addressed by cutting back on the $CaCl_2$ addition rate to the sinter mix. It was found that stable, continuous filter operation could be obtained at about 66% of the desired addition rate. Particulate collection performance was also within limits of 110 mg/Nm^3:

Sinter Plant B at Vanderbijlpark

Volume:	$110 Nm^3/sec$ (360,000 ACFM @ 300°F)
Inlet loading:	586 mg/Nm^3
Outlet loading:	110 mg/Nm^3 @ 60KV 200 mg/Nm^3 @ 0KV
Power:	60KV @ 3-4 ma per ES1000

Through discussions with CPC, it became apparent, however, that notwithstanding other observations to the contrary (e.g., media lift pipe pressure drop), that much less than the desired media recirculation rate was actually occurring in the filter. The problem was traced to the different aerodynamic characteristics of the larger, flatter South African media than the smaller, rounder U.S. media. (See Figure 5.1).



DESIGN FILTER MEDIA

ACTUAL FILTER MEDIA

Figure 5.1 Photo of Design and Actual Filter Media for ISCOR's ELECTROSCRUBBER Filters

Since appropriate media reciculation rate (more accurately, dust rate/media rate ratio) is critical in preventing dust buildup, CPC suggested some operational changes to the media recirculation system which raised the rate to design values.

It was necessary, however, to recalibrate the media flow vs. lift pipe pressure drop at a higher lift air flow in order to obtain sufficient air for the lift pipe. This required the reallocation of the air supplied by the individual blowers and the use of a supplementary blower for counterflow air and other smaller air requirements. By this means a design media circulation rate could be maintained.

After startup with this modification it is now possible to operate the ESF units up to 950 Mg/Nm^3 dust input at design gas throughput with an outlet loading of 104 Mg/Nm^3 at 190 mm pressure drop.

The collected dust is easily separated from the recirculating gravel but is still creating handling problems due to its fine particle size and caking properties once it leaves the baghouse.

With more experience in the handling and disposal of this dust, these problems will be overcome and with further adjustment of operating parameters it should be possible to achieve higher inlet loads and ultimately the design loading.

6.0 CONCLUSIONS

Several conclusions may be made regarding ISCOR's use of the ELECTROSCRUBBER Filter on its alkali-controlled sinter plant:

1. It has been demonstrated that the ESF collects high resistivity fine particulate in sinter plant waste gas at reasonable pressure drop in the dry state. It so happens that the collected dust also has commercial value as fertilizer.

2. The use of gravel as a collector holds great advantage for processes such as sintering where plant upsets could very easily cause extensive damage in other types of collectors. The use of gravel filters on further applications is under consideration.

3. The ISCOR-developed alkali removal process for sinter would not have been viable if the gas cleaning cost had been too high. The ELECTROSCRUBBER Filter solves the cost problem and also provides a clean stack emission.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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2. Alkalis in the Blast Furnace, J. Davies, J. T. Moon, and F. B. Traice, Iron Making and Steel Making, 1978, No. 4, p. 151-161.

3. Reduction of Alkaline Elements in Iron Ores by Means of Calcium Chloride Additions During Sintering, R. Robredo, M. Sirgado, E. Ferron, W. Gerlach, Third International Iron and Steel Congress, April 16-20, 1978, in Chicago. (Ensidesa Test results)

4. Weyerhaeuser's Experience with ELECTROSCRUBBER Filters on its large wood and multifuel boilers, S. Storms, D. Price, D. Parquet, TAPPI Environmental Conference, March 3, 1983, in Atlanta, Georgia.

APPENDIX

ELECTROSCRUBBER FILTER - PRINCIPLE OF OPERATION

Conceptually, as shown in Figure A-1, the ELECTROSCRUBBER Filter consists of a cylindrical vessel containing two concentric louvered cylindrical tubes. The annular space between the tubes is filled with pea-sized gravel media. The particulate laden exhaust gas enters the filter through appropriate breeching and is distributed to the filter face by the plenum section formed by the inner louver cylinder. Dirty gas is passed through the filter media at velocities ranging from 100 to 150 feet per minute and the particulate is removed from the gas stream by impaction with the media. Clean gases exit to downstream breeching.

To prevent a filter cake from forming on the face of the filter, and the resulting potential plugging problems and high pressure drop, the filtering media is continuously, but slowly (six to 10 feet per hour), moved downward in plug or mass flow. The resulting churning action across each louver opening prevents a filter cake from forming. To provide complete cleaning of the louver face, the louvers are designed so that some of the media is pushed through each louver opening thus preventing any bridging or buildup of particulate material.

The particulate laden media is continuously removed at the bottom of the ELECTROSCRUBBER Filter where it is transported by a pneumatic conveying system to the media/particulate de-entrainment section of the system. The action of the media being transported vertically in the pneumatic lift pipe separates the particulate from the media so that the particulate can be pneumatically removed from the de-entrainment section for pneumatic transport to a particulate separation and storage silo. The clean media then drains by gravity from the de-entrainment section and is returned to the top of the ELECTROSCRUBBER Filter for recycling.

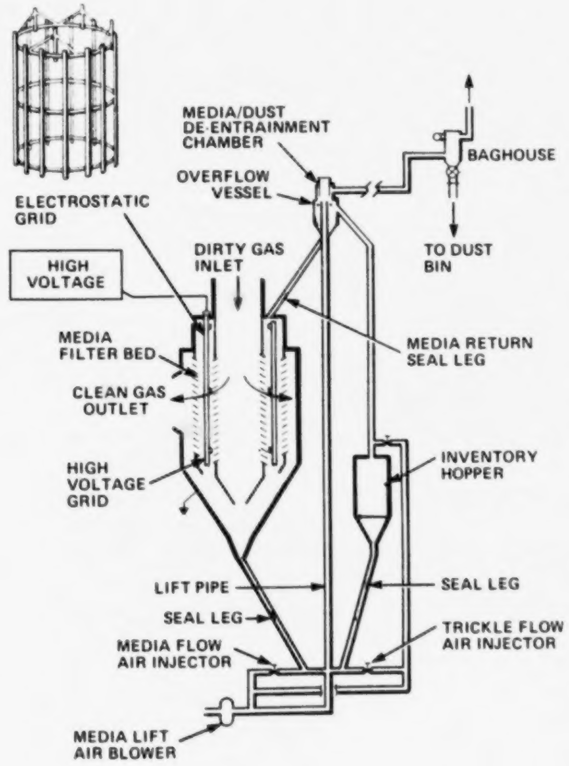
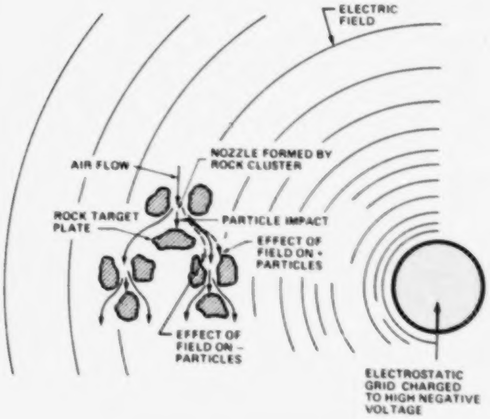

MEDIA/DUST
DE-ENTRAINMENT
CHAMBER
BAGHOUSE
OVERFLOW
VESSEL
ELECTROSTATIC
GRID
DIRTY GAS
INLET
TO DUST
BIN
HIGH
VOLTAGE
MEDIA
FILTER BED
MEDIA RETURN
SEAL LEG
CLEAN GAS
OUTLET
INVENTORY
HOPPER
HIGH
VOLTAGE
GRID
LIFT PIPE
SEAL LEG
SEAL LEG
TRICKLE FLOW
AIR INJECTOR
MEDIA FLOW
AIR INJECTOR
MEDIA LIFT
AIR BLOWER

Figure A-1 ELECTROSCRUBBER Filter Flow Schematic

The ELECTROSCRUBBER Filter module is designed to operate full of media at all times. To accomplish this, the media overflow vessel, as shown in Figure A-1, is used to assure that the freeboard section of the ELECTROSCRUBBER Filter module remains full and to eliminate any differential media flow down the two media return pipes. Excess media is returned from the media level control section by the media overflow pipe to the media inventory hopper. Media from this hopper is continuously "Trickle" fed back into the media lift pipe to provide an oversupply of media to the media overflow vessel to assure that the ELECTROSCRUBBER Filter module is always completely full of media. Air is piped from the media lift air blower into the lower portion of the media overflow pipe to provide purge air up this pipe which prevents any residual dust from re-entering the top of the ELECTROSCRUBBER Filter.

An electrical conductor, configured in the form of a cage, is positioned within the media bed of the ELECTROSCRUBBER Filter as shown in Figure A-2. A high voltage is applied to this conductor and the electrical field generated between the conductor and the inlet and outlet louvers enhances the collection of the particulate in the gas stream, greatly increasing the efficiency of the basic granular filter system (see Figure A-3). This enhancement phenomenon relies on the fact that all industrial processes produce particulate with slight positive or negative charges. Simply put, the electrical field greatly increases the probability that the particulate will impact with a piece of media in its long, tortuous path through the filter. As may also be seen in Figure A-3 electrostatic augmentation of


ELECTRIC FIELD
AIR FLOW
NOZZLE FORMED BY ROCK CLUSTER
ROCK TARGET PLATE
PARTICLE IMPACT
EFFECT OF FIELD ON + PARTICLES
EFFECT OF FIELD ON – PARTICLES
ELECTROSTATIC GRID CHARGED TO HIGH NEGATIVE VOLTAGE

MECHANICAL IMPACTION MECHANISM OF PARTICULATE COLLECTION IN A GRANULAR FILTER AUGMENTED BY ELECTROSTATIC FIELD

Figure A-2 ELECTROSCRUBBER Filter High Voltage Particulate Collection Concept

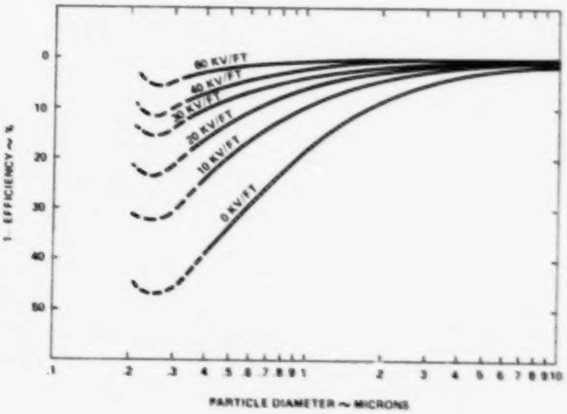


Figure A-3 Typical ELECTROSCRUBBER Fractional Efficiency as a Function of Electrostatic Grid Voltage Gradient particulate collection is especially pronounced on the fine, submicron particulate. The phenomenon is not generally affected by particulate resistivity, as would be the case with an electrostatic precipitator.

Other factors besides electrostatic grid voltage also affects fractional efficiency. For example, fractional efficiency will improve with lower gas velocities through the media panel, with "stickier" dust, with smaller media, with slower media movement velocity, and with thicker media panels. Primary filter design variables, therefore, are direction of gas flow, gas velocity, media depth, and media size. Primary filter operating variables are media recirculation rate and electrostatic grid voltage.

ROOF-MOUNTED ELECTROSTATIC PRECIPITATORS - VISIBLE EMISSIONS EVALUATION AND COMPUTER MODELLING PERFORMANCE PREDICTIONS

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ABSTRACT

Roof-mounted electrostatic precipitators are a promising technology for control of fugitive dust emissions in iron and steelmaking facilities; however, none are in use in the United States. This paper presents the results of a visible emissions performance evaluation on an electric arc furnace shop. The results are discussed with respect to Japanese furnace operating practice, and those operations are compared to U.S. practice.

During the performance evaluation, precipitator design data, test results, and particulate characteristics data were obtained for a precipitator computer modelling study. Predictions of precipitator performance were made with the EPA/Southern Research Institute computer model. The predictions are compared to previously obtained efficiency and opacity data. Performance predictions are also presented for application to basic oxygen process furnace and blast furnace casthouse fugitive dust.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

1.0 INTRODUCTION

Previous contract work sponsored by the U.S. Environmental Protection Agency has led to the identification of roof-mounted electrostatic precipitators (ESP) as a promising technology for control of fugitive dust emissions in iron and steel plants. Earlier reports[1] [2] [3] described their design and use in foreign iron and steelmaking facilities. None of these devices have been constructed in the United States. A feasibility and cost study to show its applicability to a U.S. basic oxygen process furnace (BOPF) shop was presented in a previous paper.[4]

The principal advantage of the technology is its potential for reduced operating costs through energy savings. This is accomplished by utilizing the natural thermal draft generated by hot process operations to assist air flow through the unit. Some designs operate with no fan assistance for air movement, while others require minimal fan assistance. The energy savings is significant in either case when comparing it to a fabric filter and its associated ductwork.

This paper describes a performance evaluation of a roof-mounted ESP applied to an electric arc furnace shop. The evaluation basis was visible emissions. Design data and dust characteristics data are used to make performance predictions based on computer modelling.

2.0 VISIBLE EMISSION EVALUATION

2.1 PLANT DESCRIPTION AND OPERATIONS

The Tokyo Steel plant in which this measurement program was performed is located in Hachinohe, a city in Aomori Prefecture on Honshu Island. The plant produces reinforcing bar and building steel on a plant site of 237,000 m^2 area. The raw steel production facilities consist of one electric arc furnace (EAF) of 70 tonne design capacity per cycle. However, the actual charge rate is about 100 tonnes per cycle. The plant is shut down one day per week for maintenance. On a monthly basis, the furnace capacity is 36,000 tonnes with a plant product capacity of 30,000 tonnes. The raw steel is continuously cast in a five strand caster that operates about 15 to 20 hours per day. The current average raw steel production rate is 27,000 tonnes per month with a finished product rate of 15,000 tonnes per month. The remaining raw steel is being sold to other steel finishers.

The design electrical input to the furnace is 30,000 kVA, but actual input is 36,000 to 40,000 kVA. The furnace cycle time, tap to tap, is about 95 minutes. Typically 14 to 15 heats are produced each day.

The relatively short cycle times result from several operating practices. Firstly, scrap is preheated prior to charging to the furnace. The scrap preheat is accomplished by passing the hot furnace waste gas stream through a charging bucket containing the scrap. Scrap is charged to the furnace in three batches. The first charge is about 45 tonnes; the second is 35 tonnes; and the third is 20 tonnes. Each of these batches is preheated for about 20 minutes prior to charging. The charge material is mostly automobile and heavy scrap. Secondly, oxygen-fuel (OF) burners are used to increase the rate of scrap melting in the furnace. Three burners rated at 500 liters per hour each are used. Thirdly, pure oxygen is used to cut scrap added to the furnace after the third scrap charge.

2.2 AIR POLLUTION CONTROL SYSTEMS

The electric arc furnace was constructed with a direct shell evacuation system for fume control during melting and refining operations. The evacuation rate is about 1,300 Nm^3/min (2500 m^3/min at 250°C). Particulate control in this system is achieved by a baghouse.

As mentioned previously, this waste gas stream is used to preheat scrap. The gas stream temperature leaving the furnace is about 800°C. After initial evaporative cooling, it enters the scrap at about 400°C. The gas temperature leaving the scrap is about 130°C. Fugitive dust control for furnace charging and tapping operations is provided by a roof-mounted electrostatic precipitator (REP). The REP is located above the furnace as shown in Figure 1. Partition walls attached to the roof trusses, and a sealed roof form a hood to contain the fugitive emissions and direct them to the REP inlet. The roof areas on the opposite side of the partition walls are not sealed and are vented through natural draft ventilators.

The REP installation consists of six precipitator chambers, constructed in two groups of three adjacent chambers as shown in Figure 2. Electrically each chamber is a single section powered by an 800 mA, 80 kV RMS (120 kV peak) transformer-rectifier set.

The collecting electrodes are carbon steel with a plate to plate spacing of 400 mm. The discharge electrodes are of rigid frame design constructed from 304 stainless steel, with a wire to wire spacing of 250 mm. The "wires" are actually square rods 4 mm on a side. Total collecting plate surface area is 10,188 m^2 for the installation.

The elevation view shown in Figure 2 reveals that gas flow through the precipitator is horizontal. Turning vanes to accomplish this direction change increase the static pressure drop through the REP, making fan assistance to natural thermal draft essential. The flow dampers in the REP were set to achieve the design flow of 960,000 m^3/h without the furnace in oper-

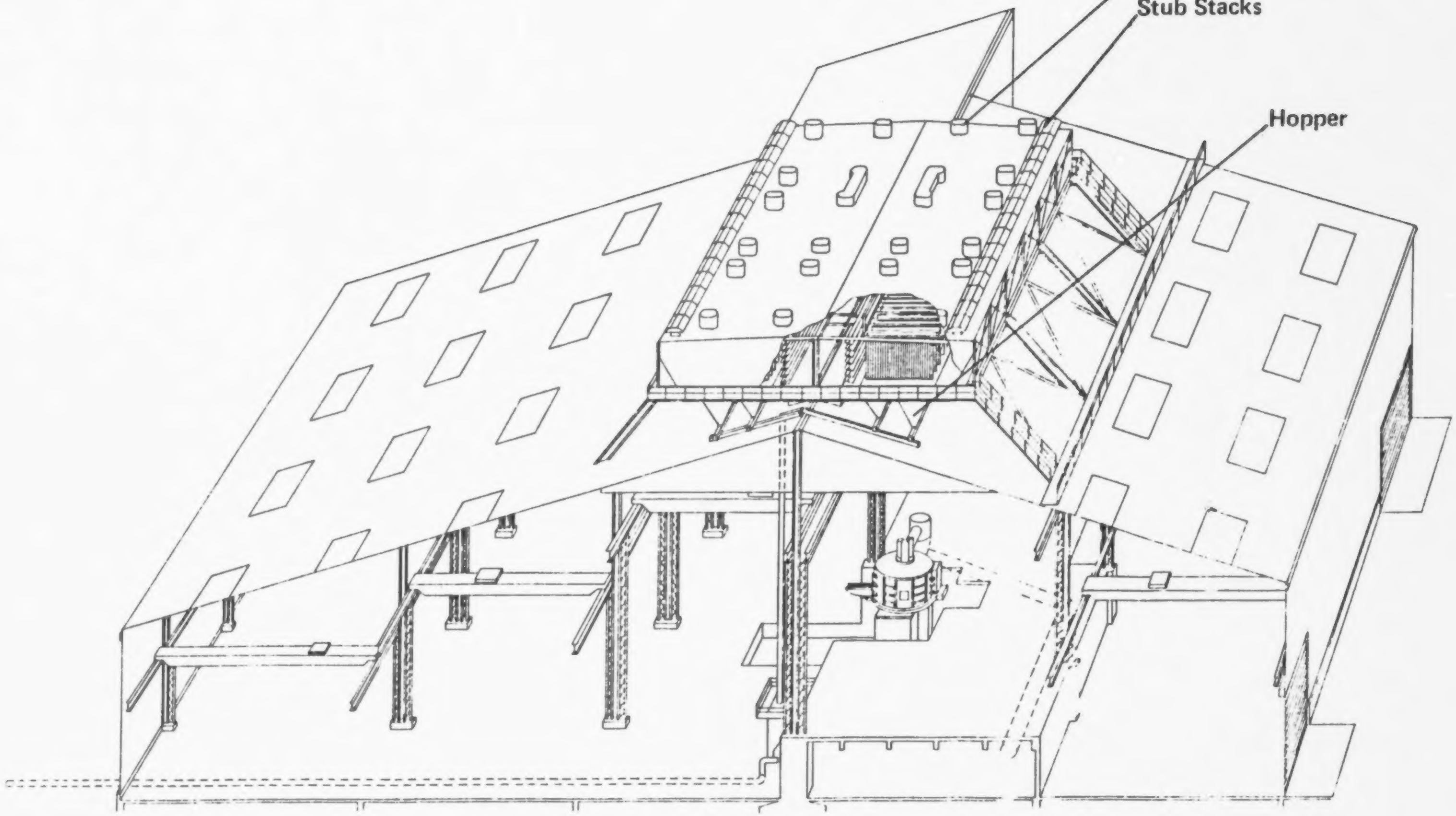
Insulator Housing
Stub Stacks
Hopper

FIGURE 1. Tokyo Steel EAF Shop

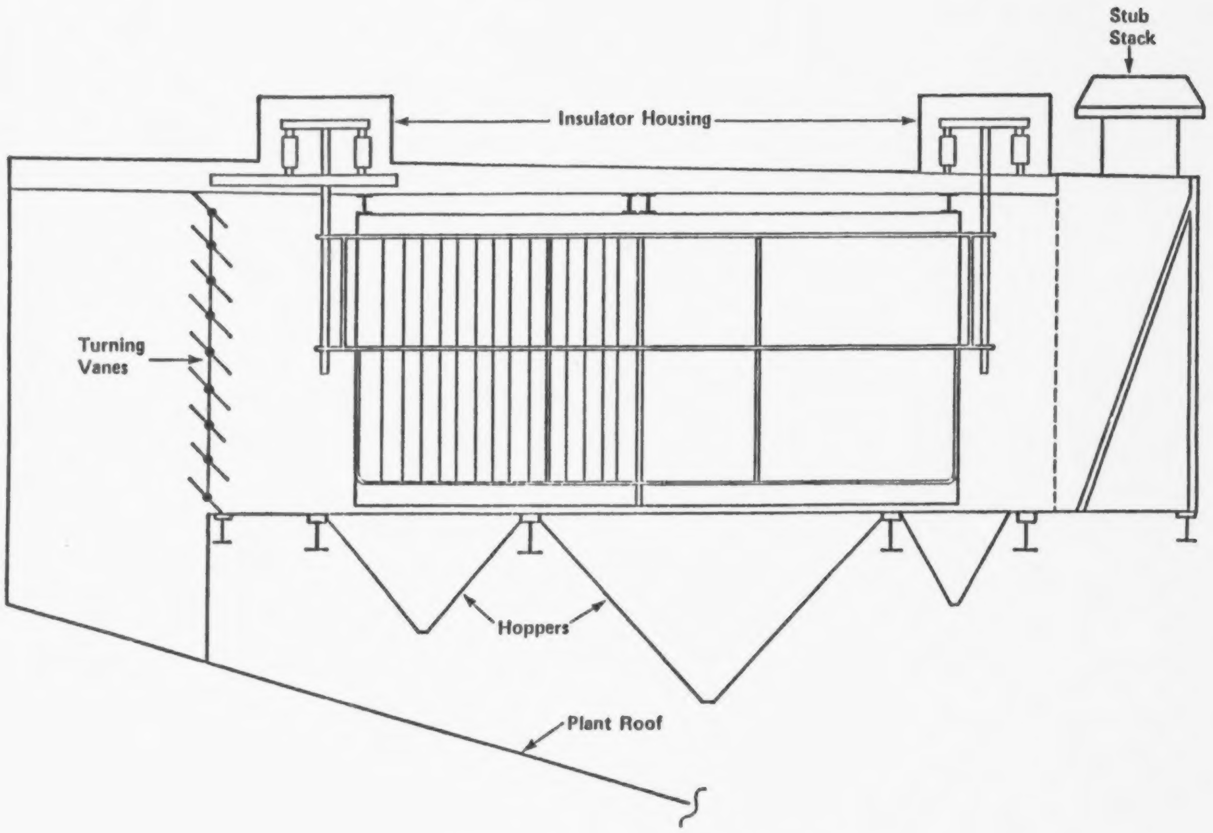
Stub Stack
Insulator Housing
Turning Vanes
Hoppers
Plant Roof

FIGURE 2. Elevation View of REP

ation. The static pressure drop through the REP has been measured at about 30 mm H_2O (1.2 in. H_2O). Propeller fans at each stub stack consume about 2.2 kWh per fan.

Dry collecting plate and discharge electrode cleaning is performed by an internal "hammer type" arrangement. The cleaning cycle time is about 5 minutes. Dust is collected in pyramid hoppers and removed by chain conveyors.

Design conditions for the REP are:

Gas flow rate - 960,000 m^3/h
Gas temperature - 30 to 80°C
Inlet dust concentration - $\leq$ 1 g/Nm^3
Outlet dust concentration - $\bar{}$0.03 g/Nm^3

Actual average inlet concentration measurements by the Japanese have varied between 0.15 and 0.5 g/Nm^3. Source instantaneous measurements have revealed inlet concentrations above 1 g/Nm^3. In 1975, the actual average outlet concentration was measured at 0.012 g/Nm^3. In 1982, the average of two outlet concentration measurements was 0.018 g/Nm^3.

Sumitomo Metal Mining attributes the increase in outlet concentration between 1975 and 1982 to increased concentrations of lead and zinc oxides in the EAF dust. In dust samples taken at both times, the measured zinc oxide concentration increased from 4% to 25%. Electrical resistivity measurements showed an increase from 2×10^{11} ohm-cm to 2.5×10^{13} ohm-cm. The outlet concentration measurements were obtained by the Japanese standard test method JIS Z 8808. The test probe was an "in-stack filter" constructed of glass. The filtering media was silica glass wool. Each measurement consisted of the average results for five stacks; i.e., one precipitator chamber. The samples were obtained at the center point of the gas stream in each stack. How these measurements would compare with EPA Method 5 measurements is not known because the efficiency of the silica glass wool (compared to a fiberglass filter) is not known, and the gas stream temperatures during the tests were not available.

Inlet dust concentrations were measured at many points across the REP entrance. Instantaneous inlets were measured with the equivalent of a U.S. high volume sampler.

2.3 VISIBLE EMISSION OBSERVATIONS PROCEDURE

Visible emissions (VE) observations were performed over a 5-day period beginning November 5, 1982. The relative elevation of the REP stub stacks with respect to the observer's locations, and the building and REP geometry permitted viewing of one set of stub stacks (15 on a side) at a time. Consideration of the sun angle and the lack of any mostly cloudy days limited the observations to the south-side set of 15 stub stacks. Because the EAF centerline was located under the south-side REP chambers, and the more concentrated emissions tended to rise directly to the south-side inlet, it may be stated that the observations were performed on the more severely challenged portion of the REP. This statement is further reinforced by the fact that the scrap preheating operation and the route of scrap charging bucket movement to the EAF (usually smoking) was located under the south-side REP.

The VE observations of the REP stub stacks were performed in accordance with EPA Method 9. Two observers simultaneously observed the same emission points recording the most opaque emissions issuing from the stub stacks. Observation positions were changed during the day to maintain an acceptable sun angle and adjust to changes in wind direction.

Concurrent with external VE observations, process data were taken and estimates of in-shop fugitive emission intensity were made. The in-shop emission intensity was characterized in two ways. First, the fugitive emissions emanating from the furnace were classified as light, moderate, or heavy. Second, every 2 minutes the opacity of emissions in the roof area around the REP inlet was estimated. Because there is no reference method for reading plume opacity inside buildings and poor lighting conditions exist at times, no significant quantitative meaning should be inferred from the latter estimates. However, the in-shop estimates can be used to indicate the relative dust load being treated by the REP at various times in the furnace cycle. Also, the REP stub stack emissions can be studied with reference to the level of inlet dust load as well as process operations occurring.

2.4 DATA ANALYSES

To facilitate analyses of VE data, the EPA Method 9 data were put into a computer file. Consecutive 6-minute average opacities were computed for each data set (each day and each observer group), beginning with the first reading of the day.

An index of REP inlet dust concentration was computed using the estimates of roof area opacity taken every 2 minutes. For the purposes of this analysis, each 2-minute reading was presumed to be the inlet opacity for the 2-minute period beginning when the reading was recorded. The index was computed by multiplying estimated opacity by the number of minutes over which it applied. For example, if the inlet opacity was estimated at 100% over the entire 6-minute period for which the outlet opacity was computed, the inlet index was 600; i.e., 6 x 100 (the maximum possible inlet index). If, as in some cases, there was not an inlet opacity estimate available for the entire 6-minute period, the index was calculated by assuming the opacity observed for a portion of the 6-minute period applied to the whole 6-minute period.

To facilitate planned ESP computer model computations, REP electrical data were recorded periodically during the test program. Transformer secondary current and voltage readings were recorded. These data were put into a computer file. Current densities and corona power were computed for each chamber of the REP for each set of readings.

2.5 DISCUSSION OF VE TEST RESULTS

About 30 hours of VE data were obtained at Tokyo Steel. Table 1 provides a cumulative frequency distribution summary of the 6-minute VE averages. As is evident, no 6-minute average exceeded 16% opacity for either observer group. Less than 1% of the 6-minute averages exceeded 10% opacity for either observer group. Approximately 5% of the averages for both observer groups exceeded 6% opacity.

TABLE 1. CUMULATIVE FREQUENCY DISTRIBUTION
Six-Minute Average Opacities
Tokyo Steel - Hachinohe Works
November 5-9, 1982

	Number of Readings Less Than or Equal		% of Readings Less Than or Equal	
Opacity %	Observer Group 1	Observer Group 2	Observer Group 1	Observer Group 2
0	108	111	35.8	37.2
1	167	174	55.3	58.4
2	203	207	67.2	69.5
3	237	235	78.5	78.9
4	254	258	84.1	86.6
5	281	274	93.0	91.9
6	287	281	95.0	94.3
7	292	290	96.7	97.3
8	300	294	99.3	98.7
9	300	294	99.3	98.7
10	300	295	99.3	99.0
15	301	297	99.7	99.7
20	302	298	100	100

Highest Average
Opacity - 16.0%

The significance of the 6% opacity level is that it is a proposed revision of the EAF New Source Performance Standards (NSPS). The proposed standard requires EAF roof monitor or building visible emissions not to exceed 6% opacity during any phases of operation.

While a direct comparison between the Tokyo Steel REP visible emission data and this NSPS scenario is one measure of the REP's potential for achieving particulate control equivalent to the best demonstrated U.S. technology, other factors must be considered as well. Among these other factors are comparison of Tokyo Steel EAF operating practice with U.S. EAF practice; design conditions for the Tokyo Steel REP as compared to actual operating conditions; and consideration of furnace operator training and its potential effect on inlet dust concentrations to the REP.

The Tokyo Steel EAF operating practice was described briefly in Section 2.1 of this paper. An initial scrap charge is followed by two backcharges all of which are preheated scrap. The third scrap charge is followed immediately by a scrap cutting operation using oxygen lances. Oxygen lances are also used during the refining period preceding tapping. The average tap-to-tap furnace cycle time during the tests was 97 minutes. The various cycle intervals are listed in Table 2. The draft Background Information Document for the EAF NSPS revisions[5] describes typical EAF cycles as 1 to 5 hours in duration, placing Tokyo Steel practice at the high rate end of the scale.

TABLE 2. TOKYO STEEL EAF OPERATION DURATIONS

Interval	Average Duration-Minutes
Cycle, Tap-to-Tap	97
Tap-Begin Charge 1	9
End Charge 1-Begin Charge 2	24
End Charge 2-Begin Charge 3	17
End Charge 3-End Scrap Cut	14
End Scrap Cut-Begin Tap	30

The practice of backcharging twice is a factor tending to increase fugitive emissions, or the particulate load to a fugitive dust control system. Use of OF burners might increase fugitive furnace emissions if they were installed subsequent to the design of the furnace waste gas system. However, because the increased waste gas volume due to OF burners represents only about 5% of the waste gas flow at Tokyo Steel, OF burners are probably not a significant fugitive emission factor. The practice of scrap cutting following the second backcharge also tends to increase fugitive furnace emissions. Fugitive furnace emissions increase during scrap cutting due to tilting of the furnace, causing misalignment between the baghouse offtake duct and the direct shell evacuation duct on the furnace. The furnace is tilted to move the pool of molten metal to the front or rear of the furnace. This speeds the melting of the scrap being cut. The degree of duct misalignment varies and may be minimized by a skillful operator concerned for the effect on fugitive emissions.

The specific furnace operating practices for those EAFs in the NSPS data base are not described in the Background Information Document. Therefore, a direct comparison is not possible. Some general comments about U.S. furnace practice may be made. At present a few EAF shops have completed or are constructing waste gas scrap preheating installations.[6] Use of OF burners is also not widely practiced. Probably less than 5% of the furnaces are equipped with these, but there may be a trend toward widespread use in domestic installations.[6] Furnace tilting following scrap charging is not known to be commonly practiced due to the risk of scrap shifting and damaging the carbon electrodes.

Presuming the Tokyo Steel scrap quality to be typical of U.S. practice (Tokyo Steel plant operators complained of having to use poor quality U.S. scrap), the other factors of cycle time, backcharging, fugitive smoke from the preheated scrap in the charging bucket, and scrap cutting with furnace tilting place Toyko Steel in a category of higher potential fugitive emissions. Consequently, Tokyo Steel represents a relatively difficult control situation for the REP.

Table 3 presents an example of the 6-minute average opacities for 1 day and by one observer group. The time column is the hour, minute, and second at which the twenty-fourth reading of the average was taken. The center column lists furnace operations and their time of occurrence. The basis for and interpretation of the inlet index has been described previously in Section 2.4.

The daily mean values of 6-minute opacities varied from a low value of 0.2% on November 5 to a high value of 2.1% on November 9. Inspection of the data for all days reveals that all the 6-minute average opacities that exceed 6% opacity occurred during the second and third scrap charges (first and second backcharges), scrap cutting, and in the period just before tapping. The two occurrences preceding tapping, on November 6 and 7, may be attributable to operator inexperience or error. The heavy furnace fugitive discharges preceding tapping on November 7 were partially a result of early retraction of the connecting duct section between the furnace direct shell evacuation duct and the baghouse offtake, in anticipation of tapping. The operator apparently expected a favorable steel sample analysis that did not occur. A similar explanation may apply to November 6, but is not known to be true. Retraction of the connecting duct while the electrodes are receiving power produces a significant dust load for the REP, appearing at least as heavy as that for backcharging. Since the REP is more sensitive to sudden increases in inlet concentration than a baghouse (related to response time for electrical controls), operator training and skill is a significant factor in maintaining low REP emissions. Earlier discussion in this section emphasized operator skill in relation to controlling emissions during scrap cutting.

A number of changes in operations were made subsequent to the installation of the REP at Tokyo Steel. The design furnace capacity at the time of the REP design was 70 tonnes per cycle. The increase in furnace capacity

TABLE 3. TOKYO STEEL VE DATA

NOVEMBER 8 . 1982

OBSERVER GROUP-B/G/B

			ESP OUTLET		ESP INLET	
HR	TIME MIN	SEC	CONSECUTIVE SIX-MINUTE AVG OPACITY-%	FURNACE OPERATIONS	INLET INDEX OPAC-MIN	MINUTES OF DATA ON WHICH INLET IS BASED
8	22	45	0.2		48	5.0
8	28	45	2.1		150	6.0
8	36	45	3.5	CHARGE 3 8:29	200	6.0
8	42	45	6.5		440	6.0
8	48	45	0.8	END CUTTING 8:43	130	6.0
8	54	45	1.0		60	6.0
9	0	45	0.0		35	6.0
9	6	45	0.4		30	6.0
9	12	45	0.0		30	6.0
9	18	45	3.1	TAP 9:18-9:22	255	6.0
9	24	45	0.4	TAP 9:18-9:22	530	6.0
9	30	45	0.2	CHARGE 1 9:26	360	6.0
9	36	45	0.0		25	6.0
9	42	45	0.2		30	6.0
9	48	45	3.5		405	6.0
9	56	0	9.0	CHARGE 2 9:50-9:52	520	6.0
10	2	0	0.0		28	6.0
10	8	0	0.4		40	6.0
10	14	0	6.5	CHARGE 3 10:09-10:11	375	6.0
10	20	0	0.8		383	6.0
10	26	0	3.8	END CUTTING 10:24	478	6.0
10	32	0	3.1		443	6.0
10	38	0	1.0		275	6.0
10	44	0	0.0		98	6.0
10	50	0	2.9		353	6.0
10	56	0	3.5	TAP 10:54-10:56	560	6.0
11	2	0	0.2	CHARGE 1 11:00-11:02	239	6.0
11	8	0	0.0		30	6.0
11	14	0	0.0		30	6.0
11	20	0	0.0		31	6.0
11	26	15	3.1		150	6.0
11	32	45	5.4	CHARGE 2 11:27-11:28	185	6.0
11	38	45	0.0		55	6.0
11	44	45	1.3		115	6.0
11	50	45	4.0	CHARGE 3 11:46-11:47	420	6.0
11	56	45	2.1		250	6.0
12	2	45	6.9	END CUTTING 11:59	485	6.0
12	8	45	0.0		75	6.0
12	14	45	0.6		20	6.0
12	20	45	0.4		200	6.0
12	26	45	0.2	TAP 12:24-12:26	220	6.0
12	34	15	0.6		600	1.0
12	40	15	0.0		---	---
12	46	15	0.2		---	---
12	52	15	2.5		---	---
13	0	0	5.8		---	---
13	6	0	0.8		---	---
13	12	0	1.0		---	---
13	18	0	6.3	CHARGE 3 13:14-13:16	342	4.3
13	24	0	1.0		60	6.0
13	30	0	6.3	END CUTTING 13:28	208	6.0
13	36	0	0.0		0	6.0
13	42	0	0.2		0	6.0
13	48	0	0.0		0	6.0
13	54	0	0.0		0	6.0
14	0	0	0.6	TAP 13:59-14:04	13	6.0
14	7	30	2.1	TAP 13:59-14:04	268	4.3
14	13	30	0.0	CHARGE 1 14:10-14:18	475	5.8
14	19	30	0.2	CHARGE 1 14:10-14:18	338	4.0
14	25	30	0.0		0	6.0
14	31	30	0.0		0	6.0
14	37	30	0.6		0	6.0
14	44	0	10.4	CHARGE 2 14:43-14:45	295	6.0
14	53	0	0.8		38	6.0
14	59	0	0.4		13	6.0
15	5	15	6.5	CHARGE 3 15:02-15:03	319	4.0
15	11	15	4.2		135	6.0
15	17	15	2.7		220	6.0
15	23	15	1.3	END CUTTING 15:18	120	6.0
15	29	15	3.1		160	6.0
15	35	15	2.1		273	6.0
15	41	15	4.4		333	6.0
15	47	15	2.7	TAP 15:43-15:46	187	4.5
15	53	15	0.4	CHARGE 1 15:51-15:52	30	4.0
15	59	15	0.0		0	5.5
16	5	15	0.0		15	6.0

ESP OUTLET SUMMARY STATISTICS

NUMBER OF AVG'S	MAX AVG	MEAN	STANDARD DEVIATION
76	10.4	1.9	2.43

to 100 tonnes per cycle probably contributes to the occurrence of higher VE opacity. Specifically, the extensive scrap cutting period following the third scrap charge is likely necessitated by the effort to achieve the higher capacity. The duration of scrap cutting (average of 14 minutes during these tests) produces a long period of often heavy furnace discharges as compared to charging periods (typically 1 to 2 minutes). Also, the practice of scrap preheating, begun subsequent to initial design, leads to fugitive smoke emissions from hot scrap as the charging bucket traverses and waits in the charging aisle. Given these conditions at the time of REP design, the design could be adjusted to provide additional collection surface and gas flow capacity. Alternatively, the scrap cutting problem might be solved by design changes to the connecting section of duct between the direct shell evacuation offtake and baghouse offtake.

This test program did not include measurement of dust concentrations. Earlier particulate concentration measurements made by the Japanese were reported in Section 2.2. The 1975 tests compared favorably to the present NSPS for EAF particulate collection devices, 12 mg/dscm. The 1982 test results were higher, 18 mg/Nm^3 (about equal to 18 mg/dscm). The increase was partially attributed to increased dust resistivity by Sumitomo Metal Mining. The difference in particulate test methodology between Japan and the United States makes it not possible to clearly state that the REP has demonstrated the capability to meet the NSPS particulate device concentration. However, it can be stated that the measurements suggest the REP can attain the NSPS level with proper design.

This paper has concentrated on comparison of VE data to the proposed NSPS roof monitor opacity limit. In the context of proposed NSPS regulations, a question to be answered is whether an REP would be considered an extension of the EAF building roof or roof monitor, or a particulate control device. In the former case the REP would be subject only to roof monitor visible emissions limits. In the latter case, it would be subject to the current NSPS particulate device concentration limit of 12 mg/dscm and 3% opacity. It is also reasonable to consider that neither category strictly applies and that a special category of rules should be applied to REPs. Consideration of these questions is appropriate to avoid discouraging industry interest in what appears to be innovative, energy saving technology.

3.0 COMPUTER MODELLING OF ROOF-MOUNTED ESP

A study was undertaken to determine the applicability of the EPA/Southern Research Institute computer model of electrostatic precipitation to the roof-mounted ESP. This effort had two phases -- phase I to determine if the computer model fit the data from the roof-mounted ESP and phase II to determine if roof-mounted ESPs could provide control for other sources in the iron and steel industry. Phase II would only be undertaken if phase I were successful.

The criteria for success in phase I were: 1) electrical conditions agreed with general electrical conditions for the plate spacing and resistivity in the roof-mounted ESP; 2) predicted penetration agreed with measured penetration for usual values of non-ideal factors; and 3) predicted opacity agreed with the measured opacity.

3.1 MODEL DESCRIPTION

The ESP model predicts ESP performance in a two-step process. First an ideal collection efficiency is calculated. This ideal efficiency is then adjusted by empirical and semi-empirical factors to account for various non-ideal and un-modeled effects. The data base for these correction factors is basically data collected on ESPs operating on coal-fired boilers.

The ideal collection efficiency is calculated based on the Deutsch-Anderson (D-A) model. Several important assumptions are made in the D-A model. The computer model must be constructed in such a way as to ensure that the assumptions are not violated. The most important assumption (and the one most often neglected by those building ESP models) is that the particles all have the same constant migration velocity. This assumption requires constant electrical conditions and monodisperse particles. Since neither condition exists in industrial ESPs -- the electrical conditions vary and the particles are not monodisperse -- blind application of the D-A model is impossible.

The EPA/SoRI model satisfies the assumptions of the D-A model by first dividing the ESP into a number of small increments in the direction of gas flow. This allows the model to treat a non-ideal ESP as a series of ideal ESPs. The electrical conditions within each increment are constant; however, electrical conditions in adjacent increments do not have to be constant. The electrical conditions in each increment are calculated by rigorous solution of the field equations for wire-plate ESPs. This solution includes the effect of both ionic and particulate space charge.

The effects of particle size distribution are incorporated by doing all calculations for single-sized particles and then integrating the individual results over the particle size distribution. The number of particle diameters and the values of the particle diameters to use in the calculation depend on the particular situation.

3.2 INPUT DATA

The input data required to run the model are ESP design information (plate-plate spacing, wire-wire spacing, total plate area), ESP electrical operating data (voltage and current), particle size distribution, particulate mass loading, gas temperature, and gas flow rate. The electrical resistivity of the particulate matter, while not essential when actual electrical operating data are available, is useful. The input data are summarized in Table 4.

TABLE 4. TYPICAL INPUT DATA FOR ESP MODEL

Dust loading 0.15 g/Nm^3 (0.07 gr/acf)

Particle density 2200 kg/m^3 Mass mean diameter 4.5 μm

Geometric standard deviation 7

Electrical conditions - Voltage 62 kV, current 0.1 A

Gas volume flow rate 2800 m^3/min (9.876×10^4 acfm)

Gas velocity 1 m/s (3.2 ft/s)

Plate length 8.8 m (29 ft)

Plate area 1750 m^2 (18,890 ft^2)

Wire to plate spacing 200 mm (7.87 in.)

Wire to wire spacing 250 mm (9.84 in.)

Non-ideal factors standard cold side (Sneakage 0.05,
gas velocity std deviation 0.20)

Normal rapping emissions

Many of the input data showed considerable variability. For example, the operating voltage varied from about 54 to 68 kV. And the mass loading varied from 0.15 to 0.5 g/Nm^3 with even higher spikes. Normal operation for the modelling was assumed to be 62 kV and 0.15 g/Nm^3.

The particle size distribution also varied. The particle size distribution from three hoppers was -- front mass mean diameter = 11 μm, geometric standard deviation = 8; center mass mean diameter = 4.5 μm, geometric standard deviation = 7; and rear mass mean diameter = 2.5 μm, geometric standard deviation = 4. For the modelling study, the middle hopper size distribution was assumed to be typical. The size distribution from the front hopper is referred to as coarse, and the size distribution from the rear hopper is referred to as fine for the rest of this paper.

The effects of the variability in the input data are discussed later in this paper.

3.3 MODELLING RESULTS

The reported electrical operating conditions were in good agreement with the electrical operating conditions predicted by DuBard and Altman[7] for the resistivity and plate to plate spacing. This result was not totally expected since the DuBard and Altman correlation was developed for fly ash and for normal plate to plate spacings. The fact that the correlation for electrical operating conditions gave reasonable answers, gives confidence that the correlations can be used to estimate electrical operating conditions for other sources in the iron and steel industry.

The particulate collection efficiency results for the various inlet data are shown in Table 5. Note that the predicted and measured data are in good agreement. Also note that the predicted opacity is in good agreement with the measured opacity.

TABLE 5. SUMMARY OF CALCULATED RESULTS FOR ROOF-MOUNTED ESP

Electrical Conditions	Inlet Loading g/Nm^3	Size Distribution	Efficiency %	Opacity %
Normal	0.5	Normal	87.06	7.1
Normal	0.15	Normal	87.06	1.2
Normal	0.5	Fine	86.11	7.8
Normal	0.15	Fine	86.15	1.8
Normal	0.5	Coarse	88.24	3.8
Normal	0.15	Coarse	88.24	1.2
Excellent	0.15	Normal	89.24	0.9
Poor	0.15	Normal	85.55	2.4
Poor	1.0	Normal	85.55	14.0

Measured opacities ranged from 0 to 16%, with 99% of the observations less than 10% and 50% of the observations less than 1%. Measured efficiency ranged from 88 to 96% depending on assumed inlet loading. Measured inlet loading ranged from 0.15 to over 1 g/Nm^3.

The uncertainty in the inlet mass loading is the major source of uncertainty in the calculated results. The inlet loading is reported to vary from 0.15 to 0.5 g/Nm^3 with peaks exceeding 1.0 g/Nm^3. The effect of these variations in inlet loading is most obvious in the calculated and observed opacities. Even with this, it appears that the model predicts opacities that are in good agreement with the measured values.

Modelling over the entire range of actual electrical operating conditions gave opacity results that covered the range of reported opacities. Limited analysis of the percent of the time that a given operating condition existed, showed that the same basic histogram for calculated opacity could be obtained as was obtained for the measured opacity.

3.4 EXTENSION TO OTHER SOURCES

Now that the model has been established as reasonable, it can be used to estimate potential use of roof-mounted ESPs for other sources in the iron and steel industry. In order to provide information on dust properties, samples from a BOPF shop and a blast furnace casthouse were obtained. The laboratory resistivity of these dusts under conditions likely in a roof-mounted ESP (71° C and low humidity) was in the high 10^{11} ohm-cm range. This is not much different from that of the Tokyo Steel samples.

The correlations of DuBard and Altman[7] were used to estimate the electrical operating conditions for the roof-mounted ESP for the two dusts. The inlet particle size distribution was assumed to be mass mean diameter = 4, and geometric standard deviation = 7. The design of the roof-mounted ESP was assumed to be the same as the Tokyo Steel unit. The results of this modelling show that the performance should be very similar to that observed at the Tokyo Steel plant. The results are given in Table 6.

TABLE 6. RESULTS OF MODELLING OTHER SOURCES

Source	Assumed Resistivity ohm-cm	Voltage kV	Current Density nA/cm^2	Efficiency %	Opacity %
BF casthouse	4×10^{11}	63	4.4	87	2.4
BOPF	4×10^{11}	63	4.4	87	2.4
BF casthouse	2×10^{12}	57	2	84.75	10
BOPF	2×10^{12}	57	2	84.75	10

Calculations assume a mass mean particle diameter of 4 μm and geometric standard deviation of 7. The ESP is assumed to be a single section with a SCA of 37.7 m^2/m^3. The inlet concentration is assumed to be 0.2 g/m^3.

4.0 CONCLUSIONS

The visible emissions performance data showed 95% of the 6-minute average opacities were 6% or less, with less than 1% of the averages exceeding 10% opacity. This performance is relatively good, but not quite as good as required for compliance with the proposed NSPS for EAF building discharges; i.e., no reading exceeding 6% opacity. Analysis and comparison of the Japanese furnace operating practices to U.S. practice suggests that the Tokyo Steel practice provides a greater potential for fugitive emissions and, therefore, represents a more difficult control situation than would be typical of a U.S. plant at present. Operator training, revisions to the furnace offtake duct design, and adequate operating practice information at the time of precipitator design are potential means for improving the roof-mounted precipitator performance.

The fact that the performance of this particular REP did not achieve visible emissions levels required for compliance with the proposed NSPS does not mean REPs are not capable of achieving the required level. Given the NSPS level as a design goal, the REP design may be revised to achieve better performance through such means as increased collection electrode surface area or increased gas flow capacity.

The results discussed above show that the ESP computer model can usefully be used to investigate ESPs applied to industries other than coal-fired boilers. The model study suggests that an REP can be applied to BOPF fugitive emissions and blast furnace casthouse fugitive emissions with equal effectiveness. Additional tests of the model for various sources in the iron and steel industry are necessary to provide the same level of confidence in the model as exists in the utility industry. Such tests should include measurement of in-situ electrical resistivity and simultaneous measurement of inlet and outlet particulate size distribution and mass loading.

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SESSION 3

RCRA/MULTIMEDIA POLLUTION ABATEMENT

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APPLICATIONS OF BIOTECHNOLOGY FOR TREATING HYDROCARBONS IN STEEL PLANT SOLID WASTE

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ABSTRACT

Two processes for the microbial decomposition of petroleum hydrocarbons contaminating iron oxides in steel plant sludges have been investigated. In the first experiment, land treatment techniques developed by the petroleum industry were used to process a 24.7% (dry solids basis) oil content sludge from a hot forming mill. Kinetic data were fitted to a first-order rate expression with respect to oil concentration. The measured rate constants ranged between 1.1×10^{-3} and 4.1×10^{-3} day^{-1}. Both increased aeration and the addition of N-P-K nutrients increased the rate of oil elimination. Less than 1% of the oil loss was due to percolation; an estimated 20% was due to volatilization. A correlation was developed between the rate of oil elimination observed in the field and the rate of carbon dioxide production measured by respirometry.

In the second experiment, currently in-progress, an above-ground composting technique with artificially-introduced microorganisms is being used to treat a steel mill water treatment sludge containing 13.5% oil. After four months, the oil contents have been reduced to the 6% to 7% range in the best-performing treatments. Respirometric measurements have been used to quantify the effects of oxygen mass transport, nitrogen/phosphorus nutrient concentration, temperature and moisture content on the rate of microbial deoiling.

INTRODUCTION

In the manufacture of rolled steel products, a variety of solid wastes are produced which are principally iron oxides contaminated with lubricating and hydraulic oils and water. There are two general classes of these oil-contaminated solid wastes, i.e., scale -- relatively dry, coarse solids with oil contents in the range of 0.5% to 2%, and sludge -- wet, fine solids with oil contents of about 10% or more. A typical integrated steel mill produces on the order of 10^5 tons of scale per year, and between several thousand and several tens of thousand tons of sludge per year depending on the steel finishing processes and the wastewater treatment system.

Resource recovery of oil-contaminated scale and sludge requires separation of the solid and hydrocarbon liquid phases. Attempts to directly recycle the iron oxides with volatile hydrocarbons by sintering can cause difficult operational problems to the steel mill. Existing resource recovery technologies can be grouped into two categories, namely incineration and solvent extraction. For treating scale, both incineration and solvent processes have been commercialized, but wide application has been hindered by unsatisfactory returns on investment. For treating sludge, the technical feasibilities and economic justifications of both incineration and solvent extraction are questionable. A particular requirement for steel mill resource recovery technologies given the current financial condition of the industry is a relatively small capital expenditure. Current allocations of capital dollars favor the installation of crucial technologies for modernization, eg., continuous casting and annealing equipment.

The objective of our research has been to identify new technological alternatives to incineration, solvent extraction, or landfill disposal of hydrocarbon-containing steel plant solid wastes. During 1978, we observed microbiological activity in samples of high oil-content sludge. Experiments were then conducted which demonstrated the feasibility of removing the oil contamination by microbial destruction. In this paper, we discuss two large-scale experiments of practical biotechnologies for the elimination of waste oils in steel plant sludge, as follows:

1. Land Treatment -- decomposition by naturally occurring microorganisms in the upper zone of top soil; widely used in the petroleum industry (1); sanctioned by the EPA (2,3).
2. Composting — decomposition by artificially introduced microorganisms in above-ground windrows of oil-bearing solid waste.

MICROBIOLOGY BACKGROUND

At least 47 genera of bacteria, actinomycetes and fungi have been identified which can utilize petroleum hydrocarbons as their source of carbon (4). An overall schematic for the uptake and metabolism of hydrocarbons and other complex nutrients is depicted in Figure 1 (5).

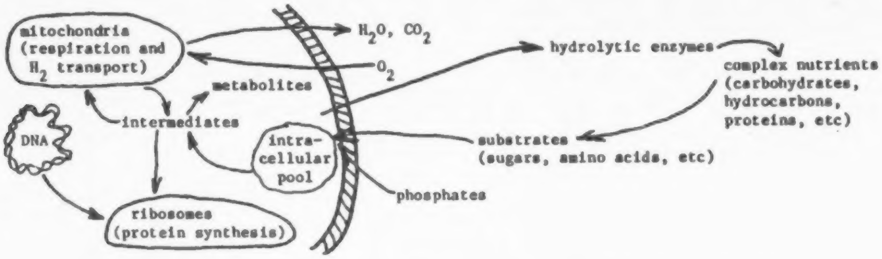

mitochondria (respiration and H_2 transport)
H_2O, CO_2
O_2
hydrolytic enzymes
complex nutrients (carbohydrates, hydrocarbons, proteins, etc)
metabolites
intermediates
DNA
intra-cellular pool
substrates (sugars, amino acids, etc)
phosphates
ribosomes (protein synthesis)

Figure 1. Overall schematic of cellular metabolism.

The stoichiometry governing the metabolism of petroleum hydrocarbon is not precisely known. Perhaps more importantly, the stoichiometry varies depending upon whether the cell is replicating or in a non-growth state. Nevertheless, approximate formulas are widely used, for example in activated sludge and single cell protein modeling, and we will use the following stoichiometry proposed by Moo-Young (6):

$$2\ CH_2 + 0.19\ NH_3 + 2\ O_2 = CH_{1.7}\ O_{0.5}\ N_{0.19}\ \text{(biomass)} + CO_2 + 1.5\ H_2O$$

For our application, the above reaction is used to convert organic compounds that are volatile in the sintering process, or organic compounds that present a threat of adverse environmental impact to CO_2 and high molecular weight biomass compounds.

In principle, the designer of microbiological processes can choose among the following three types of organisms:

- Natural strains
- Non-recombinant Mutant strains
- Recombinant Mutant strains

The specific choice depends on several factors, including availability of a mutant strain, rate and effectiveness of the desired metabolic process, cost of organism development, viability in the process environment and regulatory approval.

LAND TREATMENT EXPERIMENT

A $3x2^2$ factorial experiment was used to investigate the effects of oil concentration, nutrient addition and aeration frequency on the rate of oil degradation and unsaturated zone groundwater quality. As shown in Figure 2, fourteen 7.6 m x 1.2 m plots were prepared during September 1981 at Homer Research Labs in Bethlehem, PA. A rototiller was used to aerate the soil to a depth of approximately 20 cm. Throughout the experiment, the tilled zone oil content in each plot was measured from 5-point composite samples by chloroform extraction in a Soxhlet device. Soil pH was determined according to standard practice by slurrying. Unsaturated zone groundwater quality was monitored using pressure-vacuum lysimeters buried at depths of 1 m at the positions indicated in Figure 2. The rate of microbiological activity was measured by carbon dioxide production respirometry.

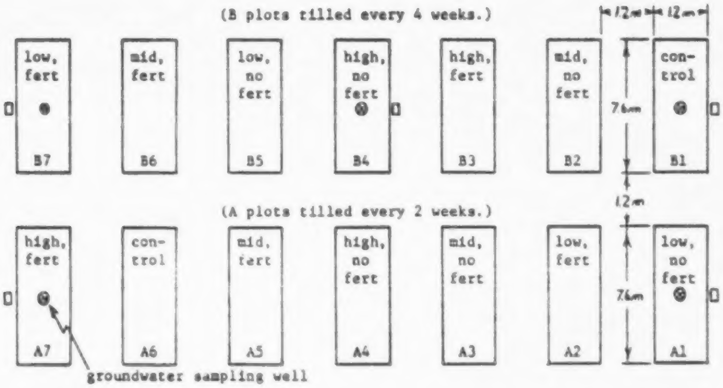

(B plots tilled every 4 weeks.)
1.2m
1.2m
low, fert
B7
mid, fert
B6
low, no fert
B5
high, no fert
B4
high, fert
B3
mid, no fert
B2
con-trol
B1
7.6m
1.2m
(A plots tilled every 2 weeks.)
high, fert
A7
con-trol
A6
mid, fert
A5
high, no fert
A4
mid, no fert
A3
low, fert
A2
low, no fert
A1
7.6m
groundwater sampling well

Figure 2. Layout of Land Treatment experiment.

In pretest soil samples, we determined the amount of chloroform extractable matter from naturally occurring organic matter ranged between 0.026% and 0.043%. The cation exchange capacity of the soil was 9.3 milliequivalents per 100 g. The soil texture was silt-loam. The soil type was a Connestoga-Hollinger complex.

Before the sludge application, 0.86±0.026 kg/plot of an 18% N - 24% P_2O_5 - 6% K_2O fertilizer was spread on the six plots scheduled for nutrient addition. In the spring of 1982, 0.93±0.028 kg/plot of the fertilizer was applied before the first tilling of the year.

The sludge sample used in the experiment contained 62.7% water, 28.1% solids and 9.20% oil. Sludge density was 1.23 g/cm^3. The oil was principally petroleum-based. Chemical compositions of the solid and oil phases, solids size consist and results of an EPA Extraction Procedure acetic acid leach are given in Table 1.

TABLE 1. CHARACTERIZATION OF SLUDGE USED IN LAND TREATMENT EXPERIMENT

Solid Phase Composition		Oil Phase Composition		As-produced Sludge EP Leachate Composition	
Fe	66.3%	As	<5 ppm	As	0.03 mg/l
SiO_2	0.9	Ba	<10	Ba	1.0
CaO	1.1	Cd	<1	Cd	<0.01
Pb	0.05	Cr	<5	Cr	0.09
Cr	0.01	Pb	43	Pb	<0.02
Cd	<0.01	Hg	<0.1	Hg	<0.002
		Se	<5	Se	<0.01
		AG	<5	Ag	<0.02
Size Consist		Fe	3100		
		Mn	100		
1 mm	0.5% retained				
74 µm	3.4				
25 µm	13.5				
Fines	100.0				

On October 7, 1981, the sludge was metered onto the the 12 working plots through a hand-carried perforated pipe distributor. The low sludge content plots received between 130 and 214 kg; the mid level plots received between 266 and 289 kg; and the high level plots received between 959 and 1066 kg (7). No change in the fluid level due to percolation was detected prior to the initial tilling. The lysimeters yielded no samples during this period. All plots were tilled three times during 1981. Regularly scheduled tillings recommenced on March 24, 1982.

Throughout the experiment, soil pH remained stable in the range of 6.5 to 8.3 with no significant trends among the plots. At no time were there any problems with odors from the land treatment plots.

OVERALL MATERIAL BALANCE

Measured Rate of Oil Elimination

Soil oil content data for the twice monthly tilled plots over 1981 and 1982 are presented in Figure 3. Other data are presented in reference 7.

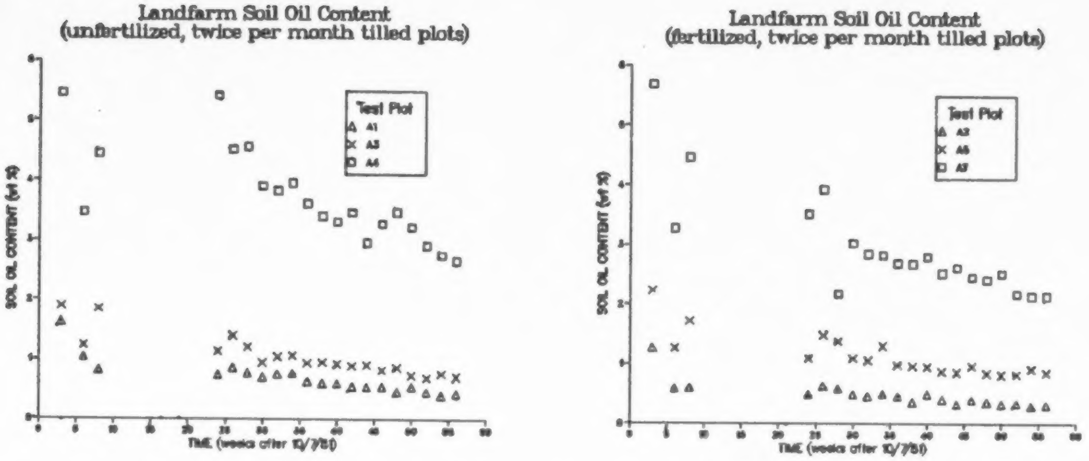


Figure 3. Soil oil contents measured in "A" land treatment plots.

An initial estimate of the rate of oil elimination was made by computing the least-squares regression lines through the March 24 to July 12, 1982 data. The measurements are listed in Table 2. These first results were in excellent agreement with published data from the petroleum industry (1). Analysis of variance showed that the linearized rate of oil elimination was affected only by the oil concentration. Non-linear analysis of the oil content data, discussed later in the paper, showed that nutrient concentration and aeration frequency also significantly affected the rate of oil elimination.

TABLE 2. MEASURED RATES OF CHLOROFORM-EXTRACTABLE MATTER ELIMINATION - 3/24/82 to 7/12/82

Plot	Elimination Rate	Plot	Elimination Rate
A1	30±4.0 g (oil)/m^2 wk	B1	0.18±0.025 g (oil)/m^2 wk
A2	19±2.5	B2	40±5.5
A3	51±7.0	B3	200±25
A4	260±35	B4	170±25
A5	54±7.5	B5	8.4±1.2
A6	4.9±0.70	B6	54±7.5
A7	120±15	B7	33±4.5

Oil Loss by Percolation--Groundwater Effects

An upperbound estimate of the total percolation flux was made by assuming that 100% of the 46 cm of rain that fell between March 24 and July 12, 1982 migrated downward. Accordingly, the upperbound estimate for the total water flux was 29 l/m^2 wk.

From October 29, 1981 to June 1, 1983, ten sets of unsaturated zone groundwater samples were obtained from the lysimeters beneath A1, B1, B4 and B7. The A7 lysimeter malfunctioned throughout the test. The total organic carbon (TOC) concentration data for these samples are presented in Figure 4. Infrared spectroscopy of extracts from the 6/3/82 A1 sample, the 4/14/83 A4 sample and the 6/1/83 B4 sample showed mixtures of aliphatic acids and esters considered typical of naturally-occurring organic matter, as the principal constituents. Trace amounts of alcohols, amines and aromatics were occasionally indicated. The 6/1/83 B4 sample showed a trace amount of aliphatic oil.

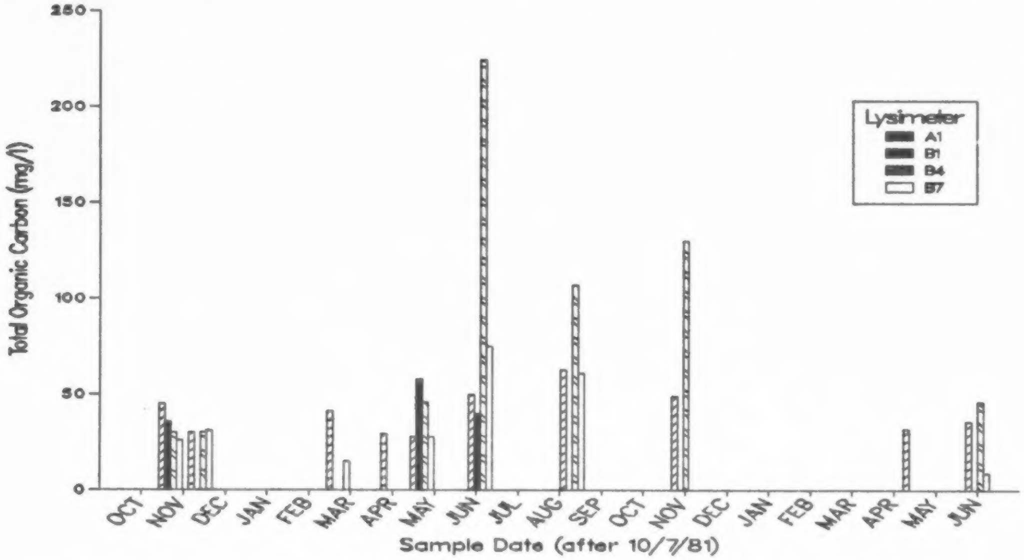


Figure 4. Total Organic Carbon concentrations in lysimeter samples.

The infrared spectroscopy data, the seasonal variations of the TOC data, and the theory describing the sorption of organic compounds by soil organic matter suggest that the dissolved organics in the unsaturated zone groundwater were principally the products of partial biological decomposition and other environmental oxidative processes, rather than the initially applied oil. The sorption of organic compounds by soil organic matter (humus) is quantitatively described by the following expression for the solute partition coefficient between the soil organic phase and water:

$$\log K_{OM} = -\log S\bar{V} - \log \rho - (1+\chi)/2.303$$

where K_{OM} is the partition coefficient, S is the water solubility (mole/liter), $\bar{V}$ is the molar volume of the solute (liter/mole), ρ is the density of the soil organic phase (g/cm^3), and χ is the Flory-Huggins interaction parameter between the solute and the soil organic matter (8). Chiou, Porter and Schmedding, using data from sorption experiments with 12 organic compounds and Woodburn silt-loam soil, established the following correlation which is claimed to be reasonably representative for many soils:

$$\log K_{OM} = -0.729 \log S + 0.001$$

With this relation, the influence of degree of oxidation on the leachabiltity of the hydrocarbons can be quantitatively assessed. For example, the solubility of n-octane is 1.7×10^{-4} moles/liter (9) which results in a predicted partition coefficient of 560. Oxidation to n-octyl alcohol increases the solubility to 4.2×10^{-3} moles/liter and reduces the partition coefficient to 54. n-Paraffins larger than octane--which are the predominant constituents of the oils in the steel plant sludge, as will be discussed in the next section--are not soluble in water and, therefore, should remain in the topsoil matrix.

An upperbound estimate for oil loss by percolation was made using the 29 l/m^2 wk estimate for the maximum water flux given above. From the analyses of the unsaturated zone water samples shown in Figure 4, the hydrocarbon content of water beneath plot B4, in excess of that beneath the control plot B1, was estimated to be approximately 60 mg/l. The upperbound estimate for oil loss by percolation was 1.7 g/m^2 wk, as compared to the 165 g/m^2 wk overall rate of oil elimination for plot B4. Therefore, according to this worst-case estimate, percolation of hydrocarbons from the applied oil could account for 1% or less of the oil loss rate. It is likely to be much less.

Further evidence for the negligible mobility of the oil was found in the soil core data listed in Table 3. The demarcation between the treatment and subtreatment zones in the noncontrol plots was sharply defined. No bulk movement of the oil downward was indicated.

TABLE 3. SUBTREATMENT ZONE OIL CONCENTRATIONS (June 1983)

Plot	Treatment Zone $CHCl_3$-extract. Content	Subtreatment Zone Sample Depth	Subtreatment Zone $CHCl_3$-extract. Content
A1	0.44%	29+1 cm	0.067%
A4	2.63	29+1	0.029
A6	0.042	29+1	0.069
B4	3.28	29+1	0.032

In addition to the total organic carbon, the chlorine and lead concentrations in the unsaturated zone groundwater (Table 4) were of interest. The presence of chlorinated hydrocarbons, such as trichloroethylene, would be indicated in the total chloride data since the analytical digestion techniques were sufficiently vigorous to decompose C-Cl bonds (10). The data in Table 4 do not indicate statistically significant differences in the total chloride concentrations beneath A1, B4 or B7, as compared to B1. Also, the infrared spectrograph of the hexane extract from the 6/1/83 B4 sample showed no indication of C-Cl bonds. The lead concentrations in the lysimeter samples have been at the limit of detection or less. Given the 7.9 to 8.9 pH range in these samples and the cation exchange capacity of the soil, the probability of solubilizing lead from this one-time application of sludge was low. Longer term trials at higher loading rates would be required to determine if lead would be solubilized from a continuous land treatment site.

TABLE 4. UNSATURATED ZONE GROUNDWATER ANALYSES

	1981 Data		1982 Data						1983 Data	
	10/29	11/18	2/19	4/1	4/21	6/3	8/11	10/28	4/14	6/1
					Total Chloride (mg/l)					
Plot										
A1	11.1	6.0	—	—	—	<1.	6.0	<1	<0.5	—
B1	6.5	—	—	—	—	<1.	—	—	—	—
B4	8.6	6.5	—	—	—	1.0	<5.0	1.3	—	<1.
B7	27.0	53	—	—	—	1.8	7.0	—	—	—
					Lead (mg/l)					
Plot										
A1	—	—	—	—	—	—	0.1	<0.2	<0.1	—
B1	—	—	—	—	—	—	—	—	—	—
B4	—	—	—	—	—	—	0.1	<0.2	—	—
B7	—	—	—	—	—	—	0.1	—	—	—

Oil Loss by Volatilization

An upperbound estimate of the hydrocarbon loss rate due to volatilization was made using a mathematical model from the literature. Studies into volatilized lubricant emissions from hot steel forming operations (11) have shown that C_{14} to C_{19} aliphatic hydrocarbons account for essentially all of the volatilized matter. C_{18} compounds were the most plentiful components -- ranging between 10.7% and 37.3%. Accordingly, the oil in the sludge used in this land treatment experiment was assumed to be 100% n-octadecane, $C_{18}H_{38}$. Therefore, the mean volatilization rate from plot A4 for early 1982 was calculated to be 46 g/m^2 wk according to the following model (12):

$$q_i = \left(\frac{D_{ei} \; C_{ig}}{\frac{2D_{ei} \; tAh_p \; C_{ig}}{M_{io}}} \right)^{1/2}$$

where A is area (cm^2), C_{ig} is the concentration of component i at the gas-liquid interface in soil pores (g/cm^3), D_{ei} is the effective diffusivity of component i through porous soil (cm^2/sec), h_p is the depth of the tilled zone (cm), M_{io} is the initial mass of i (g), q_i is the volatilization flux of i (g/cm^2 sec), t is the time from sludge application or tilling (sec). The binary diffusivity for $C_{18}H_{28}$-air was estimated using a correlation developed by Fuller, Schettler and Giddings (13). A factor of 1/2 was used to yield the effective diffusivity for transport through the porous soil, as suggested by data on benzene emissions reported by Thibodeaux and Hwang (14). The estimate for oil loss by volatilization was compared to the observed rate of oil elimination of 225 g/m^2 wk for plot A4. Therefore, the estimate for fraction of the oil elimination rate due to volatilization was roughly 20%.

KINETIC ANALYSIS

Since the initial analysis of the soil oil content data indicated that the rate of oil elimination was significantly affected by the oil concentration, the soil oil content data were reanalyzed for the entire 1982 season according to first-order kinetics as follows:

$$C = C_o \exp(-kt)$$

where C is the concentration of oil at time t (g/g), C_o is the initial oil concentration (g/g), k is the overall first-order rate constant (day^{-1}) and t is the time from measurement of C_o (day). This was a crude overall model that lumped together the effects of microbial activity and volatilization, and neglected the effects of temperature, nutrient and moisture variations. Nevertheless, the soil oil content data, as presented in Figure 5, showed a reasonable fit to first-order kinetics. The measured rate constants for the 12 treated plots are listed in Table 5. Analysis of variance of the rate constants shows the following:

1. The effect of oil concentration on k was not significant (F statistic = 6.08).
2. Increasing the tilling frequency had a significant effect on improving the rate of oil elimination (F = 58.54).
3. Nutrient addition also had a significant effect on improving the rate of oil elimination (F = 32.06).

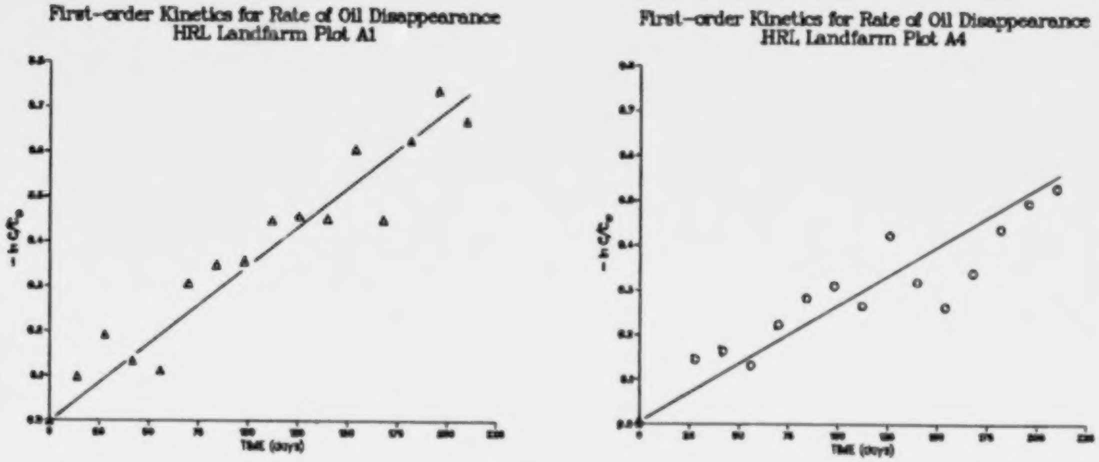


Figure 5. First-order kinetic plots for oil elimination data.

TABLE 5. MEASURED OVERALL FIRST-ORDER RATE CONSTANTS

Plot	$k \times 10^3$	Plot	$k \times 10^3$
A1	3.39 day^{-1}	B2	1.08 day^{-1}
A2	3.90	B3	1.96
A3	2.92	B4	1.27
A4	2.59	B5	2.29
A5	4.11	B6	3.12
A7	3.59	B7	2.18

RESPIROMETRY

A respirometer was constructed to measure the amount of carbon dioxide emitted from shallow static beds of soil enclosed in a sealed vessel. Soil samples were placed in 13.9 cm diameter Petri dishes filled to a depth of 2 cm. Humidified "zero air" containing <0.5 ppm CO_2 was introduced to the respirometer vessels through rotameters at 100 ± 30 ml/min. Gases exiting the vessels were dried with Drierite and magnesium perchlorate before entering Jones' bottles filled with Ascarite for quantitative absorption of CO_2 (15). A correction for the amount of CO_2 present in the "zero air" was made by comparison against a blank.

Two respirometry trials were conducted with 11/1/82 samples of soil from plots A1 (low oil), A4 (high oil) and A6 (control). The cumulative specific CO_2 production data are shown in Figure 6. The accumulated errors of measurement for all data were approximately the size of the data points on the graphs or smaller. The specific rates of CO_2 production from plots A1 and A4 were 1.3 times (0.914+0.054) and 3.4 times (2.52±0.059) that of the control (0.747±0.013 μmole CO_2/g day).

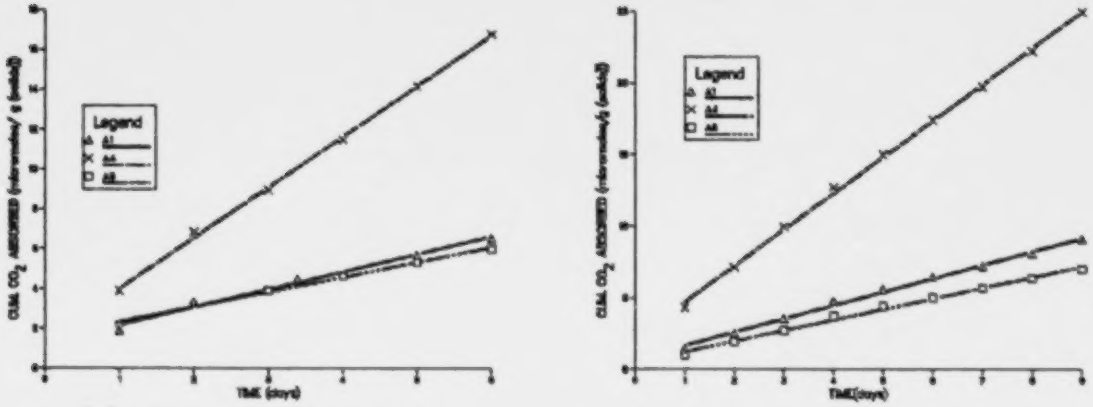


Figure 6. Land treatment experiment respirometry data.

CORRELATION OF KINETIC AND RESPIROMETER DATA

Using the measured values for k and the oil content in the 11/1/82 soil samples, the overall rate of oil disappearance in the field was estimated to be 1.49×10^{-5} and 6.99×10^{-5} g (oil)/g (soil) day for plots A1 and A4. Since about 20% of the oil disappearance was attributed to volatilization, the rate of oil disappearance due to causes other than volatilization was estimated to be 1.19×10^{-5} and 5.59×10^{-5} g (oil)/g (soil) day for plots A1 and A4.

In the respirometer samples, the amount of CO_2 produced from the decomposition of oil, as opposed to the decomposition of natural organic substances, was calculated by subtracting the A6 rate from the A1 and A4 rates. The corrected results--the exogenous respiratory rates--for plots A1 and A4 were 0.193 and 1.76 moles CO_2/g (soil) day. Finally, the biochemical stoichiometry given earlier in this paper was used to relate the amount of CO_2 produced for each $-CH_2-$ group decomposed. Assuming that one mole of CO_2 was produced for every two moles of $-CH_2-$ decomposed, we estimated the rates of oil decomposition to be 5.40×10^{-6} and 4.92×10^{-5} g (oil)/g (soil) day for A1 and A4.

The correlation of these estimates from respirometry with the rate of oil disappearance in the field is presented in Figure 7. The observed correlation is not rigorously satisfactory. A good correlation for the A4 data can be achieved if $2.25CH_2/CO_2$ stoichiometry is assumed. Despite these uncertainties, the correlation shown in Figure 7 should be useful as a rough guide to future work.

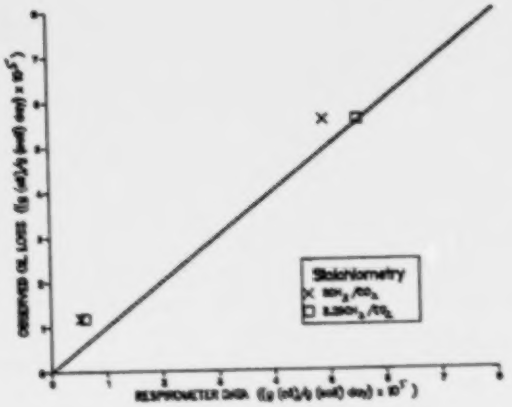


Figure 7. Correlation of respirometric data with measured rate of oil disappearance.

COMPOSTING EXPERIMENT

The effects of nutrient concentration and aeration frequency on the rates of dewatering and deoiling a steel plant water treatment sludge via above-ground composting techniques are currently being investigated. The test area is subdivided into four 1/16 acre treatment sites. Ammonium sulfate and a 46.5% P_2O_5 fertilizer are being used for nutrients. A bulldozer is used for aeration. The experimental design is detailed in Table 6.

TABLE 6. EXPERIMENTAL DESIGN OF COMPOSTING TEST

Treatment	Aeration Frequency	Nutrient Addition
1	1 wk^{-1}	none
2	1	10 N : 1 P
3	3	none
4	3	10 N : 1 P

After a series of laboratory tests, a mixed culture of non-recombinant mutant microorganisms was chosen as the inoculum.

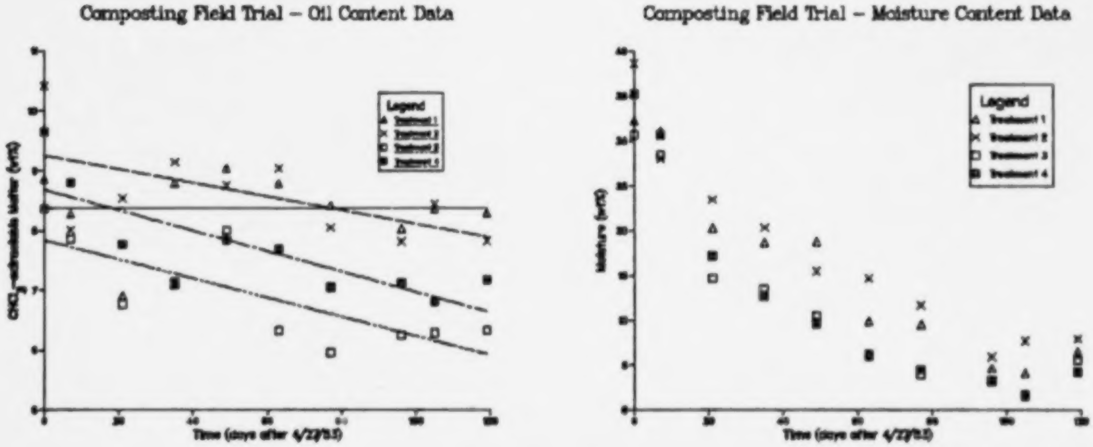
Each of the four sites contained approximately 180 tons of sludge at start-up on April 27, 1983. Initially, the sludge was composed of 47.8% solids, 44.8% water and 7.4% oil. The major portion of the oil phase was petroleum hydrocarbon with a normal amount of aromatics. A small amount of organic acid was also detected. Characterization data on the solid phase and Extraction Procedure results are given in Table 7.

TABLE 7. CHARACTERIZATION OF SLUDGE USED IN COMPOSTING EXPERIMENT

Solid Phase Composition		Solid Phase Size Consist		As-produced Sludge EP Leachate Composition	
Fe	45.2%	420 μm	0.2% retained	As	<0.01 mg/l
CaO	12.0	74	3.9	Ba	1.5
SiO	2.8	25	14.7	Cd	<0.01
MgO	1.3	Fines	100.0	Cr	<0.02
Pb	0.45			Pb	<0.02
Zn	0.31			Hg	<0.002
Cr	0.16			Se	<0.01
Cd	<0.01			Ag	<0.02

MEASURED RATES OF OIL AND WATER ELIMINATION

The concentrations of chloroform-extractable matter and water in the four treatments are depicted in Figure 8. Briefly, we can comment that the oil concentration transients agree well with our initial projections based on the microbe screening tests. The rapid rate of dewatering was, however, unexpected. The material changed to a granular consistency when the water concentration dropped below about 20%.



Figures 8a and 8b. Oil and water concentration transients in compost treatment sludge.

OXYGEN MASS TRANSPORT EFFECTS

Respirometric data from monodisperse agglomerates of 0.06, 0.15 and 1.5 mm diameters were used to determine the oxygen mass transport limitations on the rate of oil degradation. The agglomerates were collected and prepared from the 6/1/83 Treatment 4 sample. The cumulative specific CO_2 production data from these experiments are presented in Figure 9.

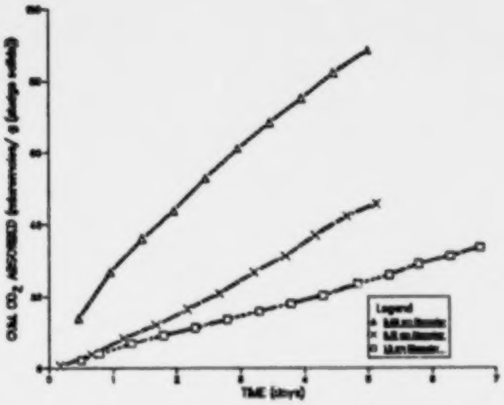


Figure 9. Respirometer data from oxygen mass transport experiments.

From these data and previous respirometer measurements, it was concluded that intra-agglomerate resistance to oxygen transport was rate-limiting. The interagglomerate bulk resistance was not limiting for practically dimensioned windrows (16).

NUTRIENT CONCENTRATION EFFECTS

The effect of total aqueous ammonia concentration on the respiratory rate was investigated using 6/15/83 Treatment 4 samples which were screened to 100% minus 40 mesh. Aqueous solutions of 10N:1P $(NH_4)_2SO_4/(NH_4)_2HPO_4$ were added to two fractions to yield 50% and 100% of the stoichiometric nitrogen requirement. Distilled water was added to a third fraction so that the moisture content in all three fractions was equivalent. The resulting CO_2 production rates in the 50% and 100% N requirement samples were 26% and 29% greater than the control.

A rough estimate for the optimum total ammonia concentration was derived by an analysis of the Michaelis-Menton kinetics for ammonia utilization according to the Lineweaver-Burke plot method (6). Ninety-five percent of the limiting reaction velocity, v_{max}, was achieved with a total ammonia pore water concentration on the order of several thousand milligrams per liter. The roughness of this estimate must be emphasized since (1) we have assumed, without sufficient proof, that the chemical activity of ammonia can be validly expressed as the calculated pore water concentration, and

(2) that the pH of the pore water remain stable (in the 8.0 to 8.5 range) so that the equilibrium distribution between unionized and ionized ammonia is similar to that in the samples used for this determination.

TEMPERATURE EFFECTS

Some insight into the effect of temperature on the deoiling rate can be derived from a careful analysis of the respirometer data from the nutrient concentration experiments. The differential CO_2 production rate plots (Figure 10) show a sawtooth variation between the daytime and nighttime respiratory rate that we believe was due to temperature fluctuations in the lab. The daytime room temperatures were measured at 23-24°C, while the nightime room temperatures rose to 27-28°C. The nighttime CO_2 production rate was about 1.2 times the daytime rate for all three respirometers.

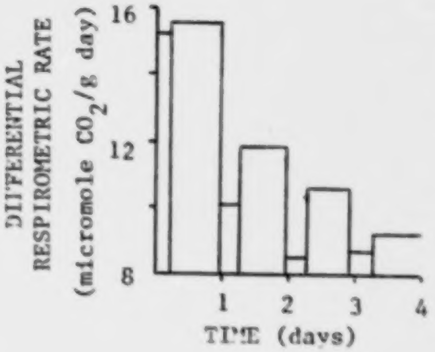


Figure 10. Differential CO_2 production rate data from nutrient concentration experiment showing daytime-nightime rate variation assumed to be caused by temperature fluctuation.

To qualitatively estimate the temperature effect, we compared the above respirometric data with well-characterized growth rate data for E. coli, a common mesophillic bacteria (17). We assume that the rate of petroleum decomposition, as one component of the cell metabolism, will be affected similarly as the rate of biomass production; however, depending on the enzymes involved, this may not be the case. Nevertheless in Figure 11, we standardized the respirometric rate at 23.5°C to the E. coli growth rate and then calculated the respirometric rates relative to the standard. Considering the uncertainties involved in producing Figure 11, any quantitative conclusions are unwarranted. However, Figure 11 gives a picture of the temperature range over which microbial deoiling processes will probably be effective and shows that the deoiling rate may vary over several orders of magnitude depending solely on the temperature.

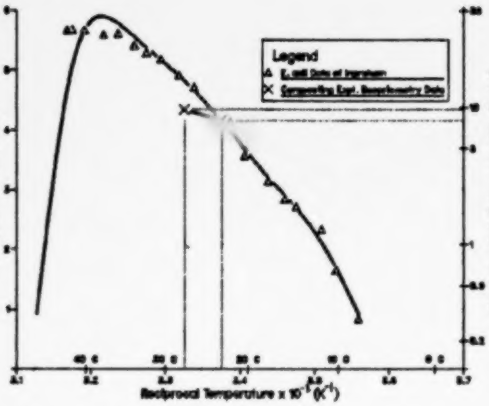


Figure 11. Qualitative examination of the effect of temperature on the rate of deoiling by inference to growth rate data for a common mesophile, E. coli (17).

MOISTURE CONTENT EFFECTS

Distilled water was added by stagewise misting to minus 40 mesh agglomerates from Treatment 4 sampled on August 1, 1983. The starting moisture content was 1.9%. The wetted sample containing approximately 9.6% moisture was rescreened and split into replicate fractions. These two fractions plus the initial screened sample were placed into the respirometers. The CO_2 production data are given in Figure 12.

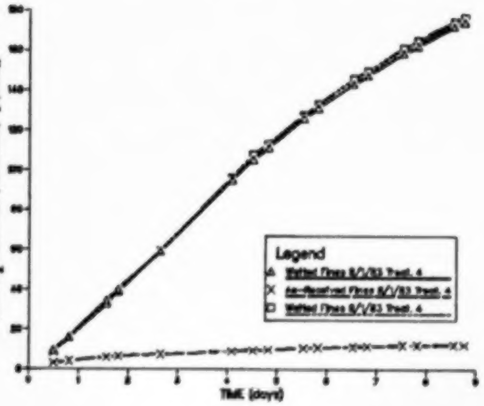


Figure 12. Respirometric data for moisture content experiment.

The importance of moisture control for process optimization is clearly illustrated in Figure 12. Proper optimization requires a balance between moisture content and agglomerate size. These parameters are not necessarily independent, and may be strongly influenced by the type of machine used for aeration.

CONCLUSIONS AND SUMMARY

Both the land treatment and the composting experiments have demonstrated the technical feasibility of large-scale microbial decomposition processes for treating hydrocarbon contamination in steel plant sludges. Based on the composting experiment results, we believe the feasibility of microbial deoiling resource recovery techology for steel plant mill scale is also established. The potential applications of these biotechnologies in the steel mills can be summarized in the following table:

TABLE 8. APPLICATIONS OF LAND TREATMENT AND COMPOSTING BIOTECHNOLOGIES IN STEEL MILLS

	High Oil-content Mill Scale	Iron-bearing Oily Sludge	Other Hydrocarbon Solid Wastes
Land Treatment			
- disposal		X	X
Composting			
- pretreatment for disposal		X	X
- resource recovery	X	X	

As an alternative disposal technology to secure landfilling, land treatment has the advantages of first, eliminating the problematical waste oil rather than storing it indefinitely, and second, being much less costly, eg. \$12-16/ton (1) as compared to \$80-100. Compared to incineration for disposal, land treatment is significantly less costly. As a disposal technology, the solvent processes do not seem appropriate since the extracted oil would still have to be treated, probably by incineration.

Regarding disadvantages, land treatment, because of the potential for percolation, must be applied with care. We believe accurate verification of treatability, such as by respirometer, chemostat, or sole carbon agar plate studies is a necessity. The proper soil type must be available to minimize hydrocarbon mobility. The absence of chlorinated organics must be verified since these substances are not readily biodegradable and, because of their polarity, may be leachable. The absence of leachable heavy metals must also be verified such as by the EPA Extraction Procedure.

The composting process holds great potential both as a means of recovering metallic resources and of pretreating hydrocarbon-bearing steel plant wastes before ultimate disposal. It is too early for us to accurately quantify the operating costs of composting, but it is clear that its capital cost advantage over incineration and solvent processes is substantial, assuming that captive land is available. Slow kinetics are the principle disadvantage. Research on optimization must proceed both on the engineering and the microbiological aspects of this technology. There is still much more to be learned about the use of natural and non-recombinant mutant strains in these applications. The promise of utilizing recombinant organisms for increasing the process kinetics is great; however, because of the well-known concerns surrounding recombinant-DNA technology, the probability that genetically engineered organisms will be used in the near future is low.

ACKNOWLEDGEMENTS

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LEAD EMISSIONS FROM WASTE OIL COMBUSTION IN STEEL PRODUCTION: A NEW CONCERN

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ABSTRACT

The significant rise in the cost of fossil fuels since 1973 has led to the increasing use of alternate fuels such as recycled or "waste oil" of various types in steel production facilities, a trend that is expected to continue for the next several years. A negative side effect of the combustion of these waste oils in such applications as boiler and blast furnace injection fuel is significantly increased emissions of lead to the atmosphere beyond what would be expected from combustion of virgin fuels such as natural gas, fuel oils, and coal.

Data developed during the preparation of the Technical Support Document to be used in the development of the Indiana State Implementation Plan for Lead quantified the extent to which waste oils were used in the four northwest Indiana steel facilities in 1982 (in excess of 50 million gallons) and the potential of waste oil use in those facilities to increase by more than 60% by 1985.

Due to its potentially high lead content (in excess of 4000 ppm by weight in some of the limited test data available), and its combustion in generally uncontrolled equipment, waste oil combustion was one of the four largest "process" sources of lead emissions in 1982 at the facilities evaluated in the study.

With the potential major increase in waste oil combustion in the near future, the increasing attention being placed on toxic air contaminants (and lead in particular) by the nation's press and federal and state environmental agencies (under the Clean Air Act and Resource Conservation and Recovery Act), as well as potential problems of attainment of the lead standard in the vicinity of major steel facilities, use of lead contaminated waste oil should be an issue of great concern to the iron and steel industry.

This paper will:

1). Quantify lead emissions from the combustion of alternate fuels such as waste oil(s), both historical and projected;
2) Compare these emissions to other sources of lead emissions in steel facilities;
3) Demonstrate the uncertainties in current data analysis;
4) Estimate the impact of these emissions on lead air quality; and,
5) Propose strategies (as necessary) to address this potentially significant source of lead emissions.

Although the information in this document has been funded, wholly or in part, by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review. Therefore, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

INTRODUCTION

HISTORICAL LEGISLATIVE AND REGULATORY BACKGROUND

Clean Air Act of 1970

The Clean Air Act (CAA) of 1970 (as amended) required the Administrator of the U.S. Environmental Protection Agency (U.S. EPA) to promulgate national Ambient Air Quality Standards (NAAQS) for five pollutants: total suspended particulates (TSP), sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3), and carbon monoxide (CO). These standards were promulgated in early 1971 and were set at levels necessary to "protect the public health and welfare". The CAA also required states to adopt a State Implementation Plan (SIP) by 1972 to attain the primary NAAQS "as expeditiously as practicable but in no case later than three years after the date of approval of such plan". Subsection (e) of Section 110 authorized the Administrator to extend the attainment date for any national standard for up to two years; thus, by mid-1975, or mid-1977 at the latest, Congress intended that healthful air quality be attained throughout the country.

As a result of a suit against the U.S. EPA by the Natural Resources Defense Council, Inc. (NRDC) in 1975, which was upheld by the U.S. Court of Appeals for the Second Circuit in November, 1976, the U.S. EPA was required to list lead (Pb) as the sixth criteria pollutant under Section 108 of the Clean Air Act and to develop a NAAQS for lead under Section 109 of the Act. It was established in the court proceedings that a lead standard was necessary to address lead health problems, particularly in metropolitan areas.

Pursuant to this judicial order, U.S. EPA listed lead as a criteria air pollutant on March 31, 1976 and proposed regulations for a lead NAAQS on

December 14, 1977. After a lengthy comment period, the final designation of a NAAQS of 1.5 micrograms of lead per cubic meter of air (ug Pb/m^3) averaged over a calendar quarter was promulgated on October 5, 1978. On the same date, regulations were also promulgated for the revision of the State Implementation Plans to include lead as required under Section 110 of the Clean Air Act. These SIP revisions were required to be submitted to U.S. EPA by July 5, 1979. The attainment date required for the lead NAAQS was October 8, 1981.

Recent Developments re: Lead SIP's

Clearly, not all states responded to this requirement and, in fact, many states still have either not obtained approval for their lead SIP or, in some cases, have not completed development of such a plan.

On July 30, 1982, NRDC re-entered the lead SIP controversy by filing suit to force U.S. EPA to adopt lead SIP's in states without such approved plans. Acting under this "threat", EPA has recently taken a much more active role in encouraging the remaining states (27 total) and the District of Columbia to complete and submit an approvable plan for attaining and maintaining the lead NAAQS. Pacific Environmental Services, in the winter of 1982, was contracted by U.S. EPA, Region V to assist the State of Indiana in the development of their lead SIP. Our research resulted in a Technical Support Document (i.e., background research) which has recently been submitted to and will be used by the Indiana State Board of Health, Air Pollution Control Division (IAPCD) in preparing their SIP .

As of the writing of this paper, U.S. EPA and NRDC have just recently agreed to a settlement of the latest NRDC suit which requires the remaining states without approved SIP's to submit plans, and U.S. EPA to act on them, on a staggered schedule over the next 4 to 18 months, or the Agency will proceed to adopt federal plans for the states which do not meet the deadlines. The 27 states (and the District of Columbia) which are affected by this order include the steelmaking states of Alabama, California, Illinois, Indiana and Pennsylvania, among others.

The Resource Conservation and Recovery Act of 1976

The Resource Conservation and Recovery Act (RCRA) of 1976 (as amended) requires the U.S. EPA to address any potential harm to human health and the environment from the improper management of hazardous wastes. As part of its continuing effort to determine whether specific and non-specific industrial residuals should or should not be listed as hazardous wastes, waste oils have been selected for study and potential regulation under Section 3001 of RCRA. At the present time, the Waste Characterization Branch, Office of Management Analysis and Information, Office of Solid Waste of the U.S. EPA may propose such a regulation for waste oil within three months. This proposed regulation under Part 261 of Subtitle 40 of the Code of Federal Regulation (40 CFR 261) could subject waste oils, when discarded or disposed of (due to their frequent contamination with toxic metals, such as lead, as well as hazardous organic constituents) to the specific management standards currently contained in 40 CFR 122-124 and 40 CFR 262-265, as well as the notification requirements under Section 3010 of RCRA.

40 CFR 261.24, the Characteristic of EP Toxicity, set maximum concentrations for lead in extracts of any waste. The analytical test methods to be followed specify treating a liquid waste as the extract if it passes through a 0.45 micrometer filter, with other specific requirements. The liquid waste could then not contain greater than 5.0 grams of lead per liter of waste, (i.e. 5000 ppm lead), in order to avoid regulation under RCRA as a hazardous waste. If a waste oil did not contain less than 5.0 grams lead per liter, then it would be subject to the management regulations and the reporting requirements mentioned above.

In addition, the Used Oil Recycling Act of 1980 specifically amends RCRA with the addition of Section 3012, which states:

> "Not later than one year after the date of the enactment of this section, the (U.S. EPA) Administrator shall promulgate regulations establishing such performance standards and other requirements as may be necessary to protect the public health and the environment from hazards associated with recycled oil. In developing such regulations, the Administrator shall conduct an analysis of the economic impact of the regulations on the oil recycling industry. The Administrator shall ensure that such regulations do not discourage the recovery or recycling of used oil."

The Technology Branch of the Hazardous Industrial Waste Division of the Office of Solid Waste, U.S. EPA is conducting this study. It has completed air emission studies from non-industrial (greenhouses, offices, apartment buildings, etc.) boilers utilizing waste oil as fuel. Proposed regulations for these non-industrial users will probably be based on toxicant limitations on the oil available to these users. Regulations for industrial users are scheduled for future development, and will consider process design as well as oil composition as a management standard basis.

LEAD EMISSIONS FROM STEEL PRODUCTION

PRIMARY SOURCES OF LEAD EMISSIONS

The primary sources of lead air emissions from steel production are blast furnace operations (both from the stoves and cast houses), the basic oxygen furnace process, sinter plant operations, open hearth furnaces, and the combustion of lead contaminated waste oils or "chem-fuel" (in boilers or as injection fuel to the blast furnaces). The magnitude of estimated lead emissions from each of these operations, or sources, is a function of the emission factor or lead content (for fuels) used, the process weight rate, and the type of control equipment and associated efficiency applied to the exhaust gases. In the sections which follow, the range of variables utilized in the Indiana SIP development work will be described and the emissions of lead from a typical steel production facility will be quantified.

LEAD EMISSION ESTIMATING PARAMETERS BY SOURCE TYPE

Blast Furnace Stoves

The emission factor used for estimating lead emissions from blast furnaces was taken directly from EPA's AP-42, Appendix E* and was equal to 0.124 pounds of lead emissions (uncontrolled) per ton of hot metal charged. The process rates for the four Indiana facilities were in the 2 million to 5 million tons per year range and control efficiencies for the stoves were estimated to be 99.5% or greater at all facilities.

Blast Furnace Cast Houses

The emission factor used for this process was provided by U.S. EPA, Region V, and was 0.00162 pounds of lead emission per ton of hot metal charged. PES' understanding is that the factor was calculated from the process fugitive particulate emission factor for cast houses and the lead content of captured particulate. Again, the process rates were in the 2-5 million tons per year range. Control efficiencies utilized for the 1982 calculations were assumed to be 0% (i.e. no control equipment) for all cast houses with the exception of Inland Steel Corporation's Blast Furnace Cast House No. 7 (which was defined, by IAPCD, to have 98% control efficiency). For the 1985 calculations, 90% control efficiency for the cast houses at the Inland (other than No. 1) and Jones & Laughlin facilities was assumed per IAPCD direction (in light of recent court settlements).

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*Compilation of Air Pollutant Emission Factors, Third Edition AP-42 (PB 83-126557), U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, North Carolina, Supplement 13, August, 1982.

Basic Oxygen Furnaces (B.O.F.)

An emission factor from AP-42, Appendix E* of 0.2 pounds of lead emissions per ton of steel was utilized. Process weight rates ranged between 4 and 6+ million tons per year. Emission control efficiencies assumed for 1982 and 1985 were 99.0% or better.

Sinter Plants

Per Appendix E of AP-42*, the emission factor used was 0.13 lb/ton for each of the wind box and vent discharges. Production rates ranged from less than 1 million to greater than 3 million tons per year. Control efficiencies assumed, per IAPCD, ranged from 80% to 99.9%.

Open Hearth Furnace

Per AP-42, Appendix E*, the emission factor utilized was 0.14 lb/ton. The production rate was again in the over 1 million tons per year range and a control efficiency of 90% was utilized.

Combustion of Waste Oils

Waste oil combustion was the single most difficult process for which to estimate lead emissions due to the variety of fuel categories and sources; lead contents in the fuels (estimated, claimed and tested); their use in boilers, blast furnace stoves, and other combustion devices; the variety of emission control efficiencies claimed for the various combustion devices; and the significant differences in quantities used by each facility.

The primary types of alternate fuels used are categorized as waste oils and as "chem-fuel", a waste product from the petro-chemical industry. The waste oils, in turn, are derived from such diverse sources as oil recovery firms, used lubricant oils from within the steel production facility (from casting and/or rolling operation, or from trucks and other internal combustion vehicles), or directly from other waste oil generators.

Of course, the source of the oil is one of the variables that can profoundly affect the lead content of the waste oil. The initial value used in our calculations was obtained from AP-42*. The EPA "default" value was 1% (or 10,000 ppm) lead by weight in waste oil. This factor, when combined with millions of gallons of waste oil combusted in uncontrolled boilers generated such large lead emissions (hundreds of tons per year at some facilities) that the IAPCD undertook a short term testing program to develop new, improved lead content numbers for further use in our study. The data collected by facility and type of fuel is summarized in Table 1 below. As can be seen, the waste oil lead contents measured ranged between 42.9 ppm and 317.2 ppm, substantially below the 10,000 ppm values originally used. On the other hand, the 3400 ppm average lead content for the chem-fuel burned at J & L was substantially greater than original J & L and IAPCD estimates of 25 ppm.

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*Ibid.

In addition to the variability in test results for multiple samples, test results on split samples have also shown substantial variability when different labortories have done the test. For example, a split sample was taken at American Recovery. Indiana's test result was 42.9 ppm (see Table 3); American Recovery performed their own test with a result of 17.7 ppm.

Table 1.

LEAD CONTENT IN WASTE OIL (PPM)
DURING WEEK OF JUNE 6-10, 1983

FACILITY	SAMPLE NO.	TYPE	LEAD CONTENT	AVERAGE	NO. USED IN CAL.
J & L Steel	1.	Waste Oil	312.8	157.7	160
	2.	Waste Oil	124.9		
	3.	Waste Oil	178.1		
	4.	Waste Oil	112.9		
	5.	Waste Oil	59.7		
	6.	Chemical Fuel	3482.4	3,399.7	3,400
	7.	Chemical Fuel	2684.9		
	8.	Chemical Fuel	4031.8		
Inland Steel	No sample since no oil is burned at present.				
U.S. Steel	1.	Waste Oil	256.9	287.1	290
	2.	Waste Oil	317.2		
Bethlehem Steel	1.	Waste Oil	Not Detectable	0.0	0.0
American Recovery	1.	Waste Oil	42.9	42.9	42.9

As can be seen, the significant variability between test results was offset, in part, by utilizing average results for each facility in the calculations for the lead emission inventory in the Technical Support Document. However, as will be discussed later, this variability in test results (particularly with so little data) does not lend much confidence to the particular emission values obtained in terms of maximum potential emissions.

As noted previously, waste oil fuel has historically been burned in a variety of combustion devices including boilers, blast furnace stoves, open hearths, etc. Naturally, each of these types of units (in any particular facility) are controlled to varying degrees. For the study, we utilized IAPCD data from either the Emission Inventory System (EIS) or developed by IAPCD staff for our use. The waste oil used in boilers generally had no controls, but fuel consumed in the stoves or other process units was controlled at the same level as previously noted (i.e. 99.5+% for stoves, etc.).

Finally, waste oil use per facility varied from a low of 0 gallons per year (at Inland) in 1982 to a high of more than 47 million gallons (waste oil and chem-fuel combined) at J&L. 1985 projections were for significant increases in waste oil use at the three facilities currently burning it, along with Inland being projected to begin waste oil combustion by 1985.

LEAD EMISSIONS FROM A "TYPICAL" FACILITY

In order to provide some confidentiality for the data obtained for the Indiana Lead SIP study, the data has been combined and a "typical" steel manufacturing facility developed for purposes of illustrating the relative quantities of lead emissions resulting from waste oil combustion. Table 2 provides process data, emission factors, control efficiencies and estimated emissions for a "typical" facility.

TABLE 2. Detailed Emissions Estimates for a Typical Steel Mill

Process	Process Rate* (TPY)	Emission Factor** (lbs Pb/ton)	Control Efficiency	Emission Rate (tons Pb/yr) 1982	Emission Rate (tons Pb/yr) 1985
Blast Furnace Stoves	3.37×10^6	0.124	99.6%	0.84	1.38
Blast Furnace Casthouses	3.37×10^6	0.00162	0.0%/90.0%	2.73	0.45
B.O.F.	4.57×10^6	0.2	99.4%	2.74	4.51
Sinter Plant	1.82×10^6	0.013	93.8%	0.73	1.20
Open Hearth	0.55×10^6	0.14	98.0%	0.77	1.27
Coke Ovens	2.86×10^6	0.00035	95.4%	0.02	0.03
E.A.F.	0.15×10^6	0.22	99.8%	0.03	0.05
Fuel Combustion by Type					
Coal	0.20×10^6	0.0133	99.0%	0.01	0.02
Fuel Oil	7.90×10^6gal	0.42lb/10^6gal	--	0.002	0.003
Residual Oil	1.48×10^6gal	4.2 lb/10^6gal	--	0.003	0.005
Waste Oil	8.09×10^6gal	1.69lb/10^3gal	67.5% (avg.)	2.22	3.65
Chem Fuel	5.10×10^6gal	25.5 lb/10^3gal	99.8%	0.13	0.21
				10.22	12.78

*tons of product per year unless otherwise stated
**lb Pb/ton unless otherwise stated

SIGNIFICANCE OF LEAD EMISSIONS

Table 2 above illustrates that only a few processes in the steel production process contribute the great majority of lead emissions to the total emissions. Clearly, combustion of waste oil is one of the largest single sources for the "Typical Steel Mill". Based on the data used for the Indiana lead SIP development, the significance of waste oil combustion varies greatly between plants, depending on the volume of waste oil combusted, the unit in which it is burned, the associated control efficiency, and, of course, the lead content of the waste oil. Table 3 illustrates the range of significance.

TABLE 3. Relative Significance of Estimated Lead Emissions from Waste Oil Combustion

Facility	1982 Lead Emissions (tons/year)			1985 Lead Emissions (tons/year)		
	Waste Oil	Total	% Waste Oil	Waste Oil	Total	% Waste Oil
Inland	--	9.69	0.0%	0.08	13.24	0.6%
Jones & Laughlin	4.88	9.24	52.8%	8.03	12.30	65.3%
U.S. Steel	2.83	19.29	14.7%	4.66	31.75	14.7%
Bethlehem	--	5.25	0.0%	--	8.64	0.0%
"Typical"	2.35	10.22	23.0%	3.86	12.78	30.2%

As can be seen in Table 3, the relative significance of waste oil combustion varies from a low of zero (i.e., no emissions from waste oil combustion) to a high of 65.3% of total lead emissions at a particular facility in 1985.

POTENTIAL GROWTH IN LEAD EMISSIONS

As noted above, the significant variable which should be of most concern is that of lead content in waste oil in the absence of any control strategy (i.e., lead content standard on a statewide or per source basis, plus testing program and results tabulation), and the potential for great variability in lead contamination of waste oils. A more conservative approach to estimating lead emissions from waste oil combustion would be to utilize a potential maximum lead content in waste oils. For example, a lead content of 500 ppm could be used for all facilities. This 500 ppm is based on the maximum lead content measured in the IAPCD study (i.e., 317.2 ppm at J&L) with a 50%+ safety factor. In this case, a table similar to Table 3 could be generated with results as follows:

TABLE 4. Potential Significance of Estimated Lead Emissions from Combustion of Waste Oil Contaminated with 500 ppm Lead

Facility	1982 Lead Emissions (tons/year)			1985 Lead Emissions (tons/year)		
	Waste Oil	Total	% Waste Oil	Waste Oil	Total	% Waste Oil
Inland	--	9.69	0.0%	0.93	14.09	6.6%
Jones & Laughlin	14.25	18.61	76.6%	23.45	27.72	84.6%
U.S. Steel	4.88	21.34	22.9%	8.03	35.12	22.9%
Bethlehem	0.97	6.22	15.6%	1.60	10.23	15.6%
"Typical"	5.22	13.09	39.9%	8.58	17.50	49.0%

Table 4 demonstrates the impact on total estimated lead emissions that this more conservative approach (i.e., 500 ppm lead content) would have. It is apparent that major increases in estimated lead emissions would result, with associated impacts as demonstrated in the attainment/maintenance evaluation.

Another aspect in which lead emissions may increase at a faster rate than anticipated in the study would be in the area of consumption rates. The Indiana study presumed a growth rate of 64.6% in steel production between 1982 and 1985. For purposes of the study, an equal growth in the rate of waste oil combustion was utilized. Should the growth in waste oil utilization exceed the estimated growth rate of the steel industry (due to continued increases in the costs of primary fuels such as gas, fuel oil, and coal) additional lead air quality impacts could be expected.

Finally, increased lead emissions could also result if future waste oil combustion increases are accompanied by a broader use of waste oil in such uncontrolled equipment as boilers. As noted in Table 2, an overall average of 67.5% control efficiency was estimated for the typical facility based on current practices of the largest waste oil users to burn large quantities of the waste oil in blast furnace stoves, which have control equipment with efficiencies of 99.5% or better. Should waste oil begin to have broader uses in facilities without these efficient controls, an overall reduction in average control efficiency would be anticipated to result.

AIR QUALITY IMPACTS OF WASTE OIL COMBUSTION

HISTORICAL MONITORING DATA

Due to the project scope (and revisions therein) of the project with U.S. EPA, a thorough evaluation of monitored lead air quality data was not performed by PES. However, the following paragraphs will describe the existing lead monitoring program in the State of Indiana, as it affects the steel industry.

East Chicago Study Area - Inland Steel Company and Jones & Laughlin Steel Corporation

There are three ambient air quality monitors located in the vicinity of the steel mills. One monitor is located south of the steel mills (Central Fire Station - 405 East Columbus), another is located east of the steel mills at the Field School (Block & James). The third monitor is located at Franklin School (Alder & 142nd Street) which is southeast of the steel mills. Two additional monitors that sample for total suspended particulates are presently not used to determine ambient lead concentrations. One of these monitors is located in the Marchtown area of East Chicago. This area is "surrounded" by J & L Steel Corporation's facility. The other monitor is located south-southwest of the steel mills in the Roxanna area of East Chicago. From 1979 through 1981, both of these monitors were used to determine the lead concentrations of the ambient air in East Chicago.

U.S. Steel Corporation - Gary Works

At various times, there have been four ambient air quality monitors located in the vicinity of USS-Gary that sampled for lead. At the present time, there are no monitors in the study area sampling for lead.

Bethlehem Steel Corporation - Burns Harbor

There are no ambient air quality monitors in the vicinity of this facility which sample for lead, nor has any past sampling been performed.

Monitored Data

Table 5 details the ambient air lead concentrations monitored since 1979 at the sites noted above. As can be seen from the limited data, there have been no monitored violations of the lead standard since the third quarter of 1979 and only two monitored values in excess of 1.0 ug/m^3 since the beginning of 1980. It is believed these low values (and the decreasing trend noted) result, at least in part, from the general economic downturn in the area since 1979 and the reduced impact of lead emissions from automobiles (due to Federal regulations). The distance of these monitors from the steel mills may also limit their ability to detect the impact of increased waste oil consumption.

Table 5 Monitored Ambient Air Lead Concentrations (ug/m^3)

CITY/AREA	ADDRESS	SARROAD I.D. #	1979				1980				1981				1982			
			1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
AQCR 067 East Chicago	Central Fire Station 405 East Columbus	15-1180-001-H-02	0.86	----	2.79	1.45	0.57	0.47	1.47	0.73	0.42	0.83	0.81	0.43	0.70	0.47	0.71	0.42
	Marktown Broad and Pine	15-1180-003-H-02	1.36	----	1.42	0.50	0.45	0.45	0.60	0.38	0.35	0.69	0.47	0.45				
	Franklin School Alder & 142nd Street	15-1180-006-H-02	1.07	0.93	0.65	1.34	0.52	0.63	0.71	1.04	0.62	0.85	0.45	0.40	0.40	0.67	0.50	0.59
	Field School Block & James	15-1180-004-H-02	1.67	0.34	0.95	0.87	0.74	0.97	0.80	0.99	0.71	1.09	----	0.53	0.79	0.67	0.71	0.66
	Roxanna Pumping Station Roxanna Dr. & Walton Ave.	15-1180-007-H-02	0.46	----	0.83	0.58	0.62	0.45	0.71	0.48	0.41	0.56	0.72	0.71				
Gary	Douglas School 2700 Jackson	15-1520-014-H-01					0.57	----	0.34	0.33	0.25	0.39	0.31	0.46	0.29	0.32	0.37	0.28

═ Monitored violation of lead standard

_ Monitored value in excess of 1.0 ug/m^3

MODELED LEAD AIR QUALITY IMPACTS

At the beginning of this project, it was anticipated that a complete attainment/maintenance demonstration for lead air quality would be made for all study areas evaluated, including the four steel facilities described herein. As the project developed, U.S. EPA and IAPCD instructed PES that it was not to complete the attainment/maintenance demonstration at the end of the effort. Therefore, PES has no data to present regarding the predicted, or modeled, impacts on air quality of the emissions of lead from the steel mills discussed earlier in this paper.

However, at an earlier stage of the project, a substantial preliminary modeling effort was made with what is now considered an invalid emission inventory. For example, in the absence of better data, it utilized the U.S.EPA default value of 1% lead content (i.e. 10,000 ppm) in waste oils. On the conservative side, annual averages were predicted rather than quarterly (per the NAAQS). However, with the assumptions used at that time, extensive exceedances of the lead standard were predicted at receptor sites surrounding each of the four steel mills discussed earlier. Some of these modeled concentrations exceeded the lead NAAQS of 1.5 microgram per cubic meter (ug/m^3) by a factor of 10 to 20 times.

Since that time, the "lead content in waste oil" tests performed by IAPCD and additional discussion and negotiations with U.S. EPA and IAPCD regarding assumptions for emission points, level of control process throughputs, etc., have resulted in reducing estimated lead emissions from the steel mills by percentages of up to 96.5% (and as little as 16.1%).

In summary, at present there is no clear cut demonstration that the lead NAAQS is being attained, and will be maintained in the future, in the vicinity of the steel mills in northwestern Indiana.

CONCLUSIONS AND RECOMMENDATIONS

Despite the lack of modeling results based on the "latest, best" emission inventory data, we believe it is apparent that significant concern should still exist over the ability to demonstrate attainment and maintenance of the lead NAAQS in the vicinity of the steel mills. We further believe that the emissions of lead resulting from combustion of lead contaminated waste oils (and other alternate fuels) are major contributors to that uncertainty due to a) the current "best" estimate of the magnitude of those emissions, b) the variability in the test data, and c) the potential for significant increases in lead emissions from waste oil combustion in the future

As part of the Technical Support Document for the Indiana Lead SIP process, PES made the following recommendations to U.S. EPA and IAPCD, in part to supplement the analysis of lead ambient air quality required in the State of Indiana Lead State Implementation Plan and in part to improve the background, basic material (i.e., the State of Indiana Emission Inventory System) to provide an improved data base for future analytical projects.

1. U.S. Steel Corporation - 1985 lead emissions from the facility are expected to be 31.75 tons per year. This is in excess of the 25 tons per year guideline developed under 40 CFR 51.80. Therefore, PES recommends a complete micro-inventory and attainment/maintenance demonstration be pursued for this facility.

2. East Chicago, Indiana Study Area - When the Inland Steel Company and the Jones & Laughlin Steel Corporation facilities in East Chicago, Indiana are considered together (due to their close proximity), the facilities exceed the 25 ton per year figure in 1985. Because of this proximity and the additive effect of their impacts on ambient concentrations of lead noted in the preliminary modeling effort, PES recommends that micro-inventory and attainment/maintenance for the East Chicago Study Area be undertaken.

3. Lead Content in Combustion Fuels at the Steel Mills - Due to the significant variability of lead content in such fuels as waste oil, chem-fuel, and crankcase oil - both between and within fuel categories - PES recommends that further study of this issue be undertaken (perhaps in cooperation with the steel mills). With a measured range of 0 to approximately 4000 ppm lead (up to a quoted 10,000 ppm) and directly associated lead emissions from the combustion of these fuels, it seems reasonable to study this area in greater detail, perhaps resulting in a state regulation limiting lead content in waste oils in order to assure continued maintenance of the ambient air quality standard for lead. It is of particular importance given the possibility of substantial increases in waste oil combustion between now and 1985.

4. Bethlehem Steel Corporation - Although the facility's lead emissions do not approach the 25 tons per year guideline, concerns over the potential of significantly greater lead emissions (and associated ambient air quality impacts) lead PES to recommend that attainment/maintenance demonstrations be undertaken for this facility as well.

5. Updating and Improvement of the Indiana Emission Inventory System (EIS) - PES recognizes it is the nature of such inventories to require continuous updating and, due to problems experienced in this project, would propose that a substantial quality assurance effort be incorporated into the next update, particularly with regard to the four steelmaking facilities.

In addition, PES makes the following recommendations to the iron and steel industry as a whole and in particular to the northwest Indiana steel producers studied in this paper:

1. Lead Content in Combustion Fuels - For the same reasons as noted throughout this paper and highlighted in number 3 above, the iron and steel industry shoud be greatly concerned about this lead content issue. For those facilities who use in-house sources of waste oil and/or utilize external suppliers, now is the time to develop additional data on fuel supplied and utilized. The data should be gathered due to the potential for national, statewide or site-by-site regulations on lead content in alternate fuels. My expectation is that the industry would favor, instead, lead content limitations in purchasing specifications, test programs to check performance, and methods to address exceedences of the specifications.

2. Assistance to States in the Regulatory Process - Due to the great variability in existing and potential estimated lead emissions, the iron and steel industry must provide as much information as possible to regulatory agencies reviewing lead in waste fuel issues (Lead SIP, RCRA, etc.) to assure the correct data is used in the evaluation. Of particular value (from the PES experience) is up-to-date process throughput, control efficiency and growth projection data.

ASSESSMENT OF BLAST FURNACE SLAG QUENCHING WITH BLAST FURNACE BLOWDOWN WATER

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ABSTRACT

One inexpensive method of blast furnace wastewater disposal that results in no release of residual water pollutants is the use of blowdown water to quench hot blast furnace slag. The resulting evaporation of the water is accomplished by using energy that would normally be lost to the plant, and the results are zero discharge of wastewater from the blast furnace. A concern is that previous EPA tests of coke quenching with water containing high levels of dissolved solids indicated that this practice tended to generate high levels of fine particulate air emissions, and it is conceivable that other contaminants in the water could vaporize to create undesirable air pollutants.

Under the first phase of this project, PEDCo conducted a literature survey, developed specific goals to be reached, and designed an overall test program. The second phase involved conducting actual tests under simulated conditions. Blast furnace slag was quenched with blast furnace blowdown water in a specially designed enclosed container. The container was continuously heated to maintain quench temperatures near those encountered in the field.

A series of 15 test runs was conducted at two different slag temperatures (1100° and 1500°F)*. The results of this laboratory-scale assessment of simulated blast furnace slag quenching with mill service (baseline) water versus blast furnace blowdown water indicated that particulate emissions increase at a more pronounced rate with high slag temperatures when blowdown water is used, presumably because of its higher total dissolved solids content. Based on EPA-OSW extraction procedure (EP) toxicity tests, the

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* Nonmetric units are used in this paper for convenience. Metric equivalents are given at the end of the paper.

quenched slag was nonhazardous. Although minor quantities of organic pollutants evolved during quenching, the data showed no relationship between these pollutants and slag temperatures, slag characteristics, or water quality. Also, no correlation was found between quench water quality or slag temperature and emissions of sulfur dioxide, hydrogen cyanide, ammonia, and fluoride.

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INTRODUCTION

Blast furnace blowdown water can be disposed of in several ways. One option is to use this water for slag quenching. Because this water evaporates during the slag quenching, the discharge of this contaminated liquid stream is greatly reduced or eliminated. Effluent limitation guidelines and standards proposed by the U.S. Environmental Protection Agency designate this disposal method as Alternative I of the Best Available Technology for handling blast furnace wastewater. This report describes the results of an environmental assessment project to evaluate the air emissions arising from quenching blast furnace slag with the blowdown from a blast furnace scrubber wastewater recirculation system.

Previous studies have shown that quenching hot coke with coke plant wastewater can give rise to significant emissions. Two major differences, however, exist between slag quenching and coke quenching: 1) slag quenching does not evaporate nearly as much water as coke quenching (15 to 30 gal/ton of slag versus 150 gal/ton of coke), and 2) the contaminant level of blast furnace blowdown water is generally lower than that of coke process waters.

In the first phase of this study (1), an evaluation was made of water consumption in various slag processing methods. The three processing methods practiced in the United States involve the use of hard slag pits, expanded slag, and granulated slag. Because about 90 percent of total slag production entails the use of the hard slag pit method (in which water is sprayed on slag after it has solidified), this study focuses on this method.

The initial study revealed that alternative disposal methods for blast furnace (BF) blowdown water (e.g., for fugitive dust control or basic oxygen furnace hood cooling) were either infeasible or did not offer opportunity to dispose of significant quantities of water on an industrywide basis.

The study further revealed that the use of blast furnace blowdown water for slag quenching might result in air pollution through the release of various dissolved contaminants, including a variety of organics, during water evaporation. Because the conclusions regarding possible air pollution were based on theoretical considerations, actual testing was needed to evaluate this potential for emissions.

The quenching of hard slag, which takes place in large open pits, releases steam and emissions in fugitive form. The original sampling plan envisioned a large hood placed over such a pit for sample collection.

Further considerations proved that this approach would be too costly; also, the captured sample might not necessarily be representative because of wind currents, uneven spraying, and other factors.

Another approach considered the use of a minipit, either within an existing pit or at an unused slag runner. Such an arrangement would permit the use of a close-fitting hood to capture all the emissions. Unfortunately, none of the steel companies contacted was willing to participate in such a program.

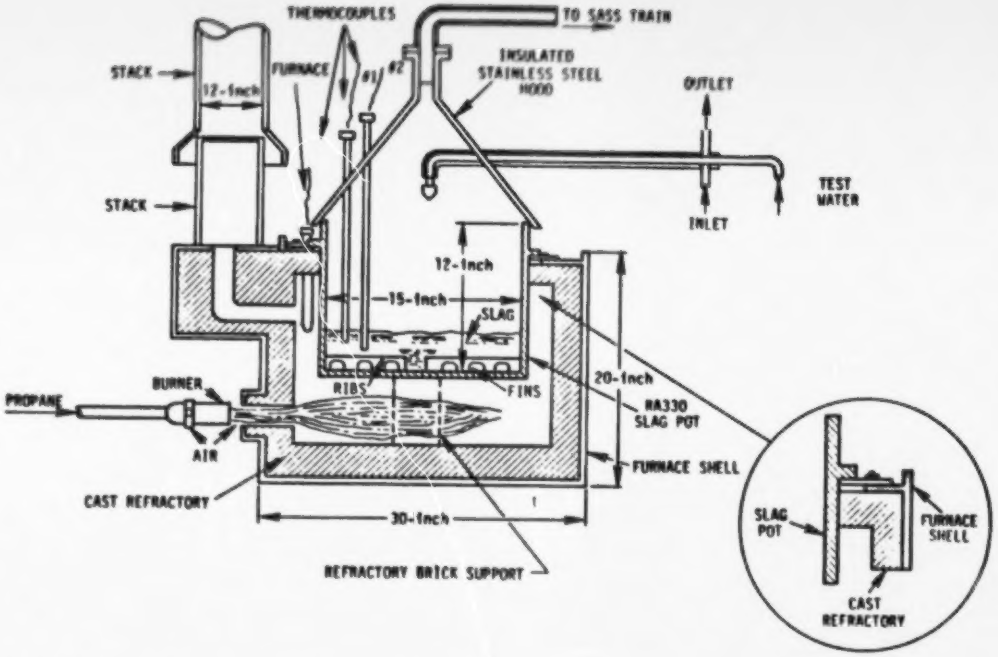
The testing approach finally selected involves simulated slag quenching in a laboratory. This approach, which entailed the construction of a furnace that would indirectly reheat fresh slag, offered the following advantages. First, all work could be done under controlled conditions, and accurate measurements could be made of slag, water, and emissions. Second, duplicate testing under a range of conditions could be made at much lower cost than in field testing. The disadvantages were that it was not possible to collect emissions from the quenching of fresh molten slag, no runoff water could be generated because of the inherent design of this approach, and the water evaporation occurred in a semisealed container, which probably excluded potential reactions with air.

About 25 pounds of slag was poured into the slag pots at a blast furnace and transported to the experimental furnace. Blowdown water was obtained from another blast furnace that had a tight recycle system and transported to the laboratory in Teflon-lined drums. Mill service water was used as a baseline for comparison. A series of 15 test runs was conducted at two different slag temperatures. These tests provided a qualitative estimate of emissions under different slag temperatures and the effect of the use of blast furnace blowdown water on these emissions.

EQUIPMENT DESIGN

Figure 1 shows the general arrangement of the experimental setup. The slag pots are designed to withstand the severe thermal stress of being continuously heated for 4 to 6 hours while the slag was simultaneously quenched inside the pot. They also had to withstand the high temperatures of the molten slag.

Figure 2 presents two photographic views of the actual setup during the test run. The slag pots were made of RA-330, a high-temperature stainless steel. The bottom of the pot was reinforced with pie-slice ribs, which also aided in heat transfer to the slag. Additional fins were provided for better heat transfer. The furnace was custom-designed. The emission capture hood was made of 304 stainless steel. A special probe was used and attached to the stainless steel connecting pipe from the emission collection hood. The probe was glass-lined and had the necessary electrical heating arrangement. A special glass filter assembly designed to hold a 6 in.-diameter Whatman filter paper was used. The inlet pipe for the blowdown water was a stainless steel pipe with a cooling-water jacket. This arrangement was selected to ensure that the blowdown water did not evaporate before hitting the hot slag surface.


THERMOCOUPLES
TO SASS TRAIN
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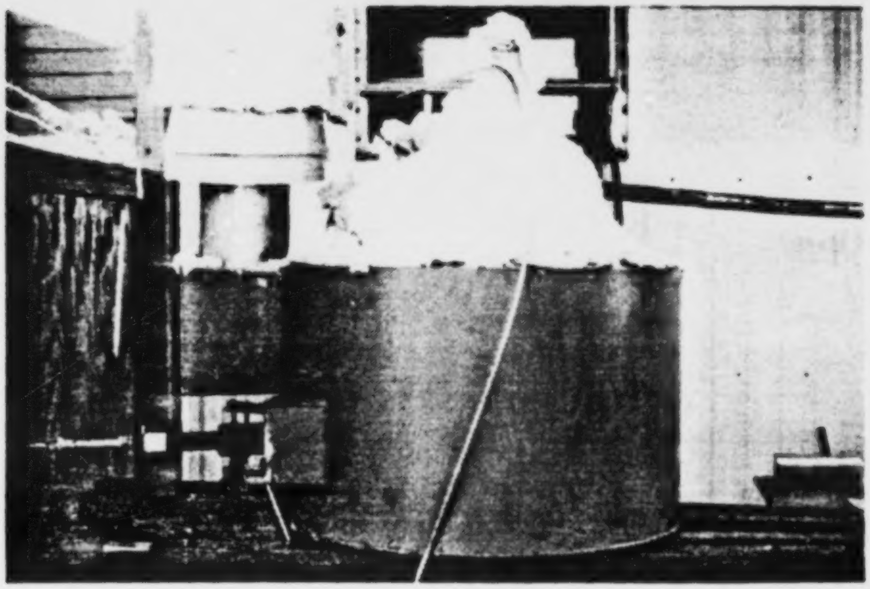
TEST WATER
INLET
12-inch
15-inch
SLAG
BURNER
RIBS
FINS
20-inch
PROPANE
RA330 SLAG POT
AIR
FURNACE SHELL
CAST REFRACTORY
30-inch
SLAG POT
FURNACE SHELL
CAST REFRACTORY
REFRACTORY BRICK SUPPORT

Figure 1. General arrangement of the experimental setup (not to scale).



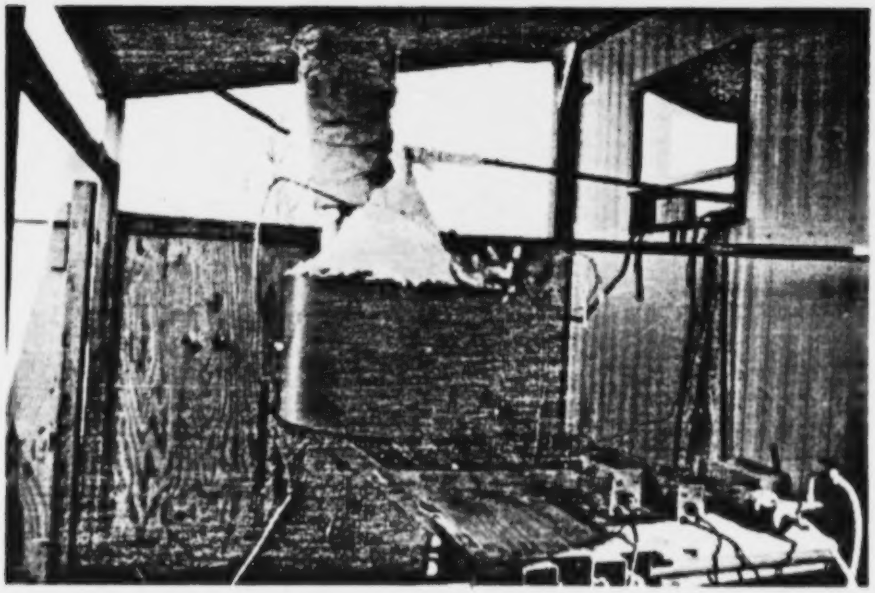


Figure 2. Two views of the actual experimental setup of slag pot and furnace.

TEST DESIGN

The main objective of the test series was to evaporate water on the hot blast furnace slag and correlate air and water discharges and slag characteristics as a function of quench water quality (baseline versus blast furnace blowdown water) and slag temperature. The blast furnace blowdown water was required to meet the BAT limitations.

The baseline water was typical mill service water obtained from a steel plant that uses well water. The water was obtained in 55-gallon Teflon-lined drums. Water samples were simultaneously collected for analysis of dissolved solids, priority pollutants, trace metals, and organics. The slag samples were obtained from the same plant. However, the blast furnace blowdown water was obtained in 55-gallon Teflon-lined drums from another plant. The blast furnace wastewater treatment system at this plant was running at a high rate of recycle (97%) with around 3 percent blowdown, which meets BAT limitations. The average blowdown was 20 gal/min during the period, which amounts to ≈15 gal/ton of hot metal. During the period of sample collection, the plant was not conducting any side-stream softening. Water samples were collected for analysis of dissolved solids, priority pollutants, trace metals, and organics. The coke used at the blast furnace during this period was quenched with coke byproduct plant wastewater makeup.

Two slag temperature ranges were selected for these tests. The thermocouples were arranged to measure the temperature 1/2 in. and 1-1/2 in. below the slag surface. The low temperature range selected was 1000° to 1100°F, and the high temperature range was 1500° to 1600°F, as measured by the thermocouple 1/2 in. below the surface. The originally selected high temperature range was 1900° or 2000°F, but this had to be modified downward because a temperature this high could not be consistently maintained commensurate with desired water evaporation rate and sample volume. Table 1 shows the sequence of sampling runs, quench water type, slag temperature, and number of slag quenches for each condition.

The slag samples were obtained from a blast furnace shop in batches of three. After the pots were thoroughly cleaned, they were taken to the blast furnace casthouse, where molten blast furnace slag was removed from the slag runner with a slag spoon during a cast. It was poured into each pot one spoonful at a time and allowed to solidify. This process was repeated until a height of ≈2-1/2 in. was reached (≈25 lb of slag). The pots were then allowed to air-cool before being transported to the laboratory. The pots were kept covered to avoid any contact with moisture until the time of the test.

In the selected test approach the slag was heated in the pot to the predetermined temperature and maintained at that temperature while the slag surface was being quenched. The emissions and steam generated during the quench were collected. This prolonged quenching period at a desired temperature allowed collection of a large volume of emissions. The extended sampling period was required because of the expected low concentrations of trace metals and organics.

TABLE 1. AIR EMISSION SAMPLING SCHEME

Quench water type	Slag temperature	No. of slag quenches[a]
Mill service water	High (≈1500°F)	3
Mill service water	Low (≈1100°F)	3
Blast furnace scrubber blowdown water	Low (≈1100°F)	4
Blast furnace scrubber blowdown water	High (≈1500°F)	4

[a] For each quench water type, one slag quench was used to collect H_2S, F^-, CN^-, and NH_3 samples. The other quenches were used to collect SASS and grab samples.

TABLE 2. SAMPLING METHODS AND ANALYTICAL PROCEDURES FOR AIR SAMPLES

Species	Sampling method	Analytical procedure
H_2O	SASS	Gravimetric
H_2S	EPA Method 11	EPA Method 11
SO_2	SASS	EPA Method 6
CO, CO_2, O_2, N_2	Grab samples	GC/TCD
F^-	EPA Method 13B	EPA Method 13B
CN^-	EPA Method 13B	808[a]
NH_3	Impinger train	801[a]
Particulates	SASS	EPA Method 5 (front-half only)
Volatile organics (C_1 to C_7)	Grab samples	GC/FID
Organics plus metals	SASS	Level 1[b]

[a] Sample method numbers taken from "Methods of Sampling Analysis," 2d Ed, American Public Health Association, 1977.

[b] IERL-RTP Procedure Manual: Level 1 Environmental Assessment (Second Edition). EPA-600/7-78-201, October 1978.

For each test, approximately 15 liters (4 gallons) of the specified type of quench water was drawn into a glass jar from the Teflon-lined drums. The water in the drum was kept agitated by the use of a 1/3-hp mixer. During the entire period of each test, the water in the jar was kept under agitation by recirculating it with a centrifugal pump to ensure that no solids would settle out in the jar. A slip stream was connected to the quenchwater inlet pipe. A spray nozzle was installed to provide uniform application of quench water. The use of fine spray nozzles was discontinued, however, because they tended to plug at test temperatures.

AIR SAMPLING APPROACH

Steam and air contaminants generated from slag quenching with the two types of quench water were sampled and analyzed for various pollutant species. The results of the mill service water tests served as a baseline against which to evaluate emissions from the contaminated blowdown water. For each type of quench water a series of tests was conducted to determine the composition of the emissions generated at the different slag temperature. Table 2 shows the sampling methods and analytical procedures followed during the test series.

A modified Source Assessment Sampling System (SASS) train was chosen as the principal collection device for three reasons: 1) the sample rate can be varied up to approximately 114 liters/min (4.0 ft^3/min), 2) a larger sample volume can be collected, and 3) the sampling train is designed to maintain a high temperature of 205°C (400°F). The SASS train was operated without cyclones. The only modifications to the SASS train were a glass-lined probe and glass filter holder, which significantly improved sample quality, especially for trace element determinations. The SASS train was operated for approximately 4 to 6 hours per run.

TEST RESULTS

The evaluation of the test data in terms of water quality, slag temperature during quenching, and slag characteristics is presented under the following subcategories: particulate emissions, hydrogen sulfide, sulfur dioxide, hydrogen cyanide, hydrocarbons C_1 to C_7 and C_7 to C_{16}, organic emissions, metals, and the toxicity of the quenched slag. All emissions except permanent gases and C_1 to C_7 are expressed in terms of milligrams or micrograms per liter of water evaporated on the slag surface during quenching. In all cases, the water evaporated is the same as the water applied. The water recovered was always less than the water applied.

Particulate Emissions

The level of particulate emissions was related to two conditions: the total dissolved solids (TDS) content of the quench water (450 mg/liter for the mill service water versus 2491 mg/liter for the blast furnace blowdown water) and the temperature of the slag. Emissions are shown in Table 3.

TABLE 3. PARTICULATE EMISSIONS

Type of water	TDS content, mg/liter	Avg. slag temp., °F	Particulates, mg/liter of H_2O evap.
Mill service water	450	1125	34.7
Mill service water	450	1523	51.5
Blast furnace blowdown water	2491	1116	156.8
Blast furnace blowdown water	2491	1633	395.2

Figure 3 indicates the above results in a graphical form, assuming a linear TDS particulate relationship based on coke quench test data.

In normal BF slag quenching practice, as the slag surface cools down with time, part of the applied water evaporates and the rest either runs off or enters into crevices formed during quenching, and the overall rate of evaporation declines. During these test runs, on the other hand, the slag was continuously heated to keep the surface temperature high, which eliminated the possibility of any runoff water. Particulate emissions may be higher than those encountered in actual practice because during quenching water droplets are instantaneously converted to steam on the hot slag surface, which creates a shattering effect. This effect is more pronounced at higher slag temperatures, which may account for the higher particulate emissions at these temperatures. During the tests, the slag surface had a grayish-white color after quenching, and the surface was finely pitted as opposed to the uniformly smooth surface of air-cooled slag. During normal slag quenching operation, the surface runoff may reduce some of the particulate emissions caused by explosive shattering.

Visual examination of the inside surface of the collection hood showed hard water deposits on the nozzle and the inside surface of the hood at the end of all test series. No attempt was made to recover these deposits, which probably would have become additional particulates had they not adhered to the hood. Those found in the closed hood would tend to offset carryover of particulates with runoff water that would normally occur during normal hard slag quenching operations. Also, less material may have condensed on the hot hood at high slag temperatures. Conversely, steam impingement on a hotter hood would be more likely to evaporate and leave any particulate as a deposit on the hood.

Table 4 compares particulate emissions during slag quenching with those during coke quenching. The coke quenching data are derived from Dofasco No. 1 wet quench tower tests (2) and U.S. Steel Lorain tests (3).

Figure 3 shows that emissions increased as quenching temperature increased from 1100° to 1500°F. If emissions at 2200°F were projected linearly, they would be 75 mg per liter of water evaporated for clean water

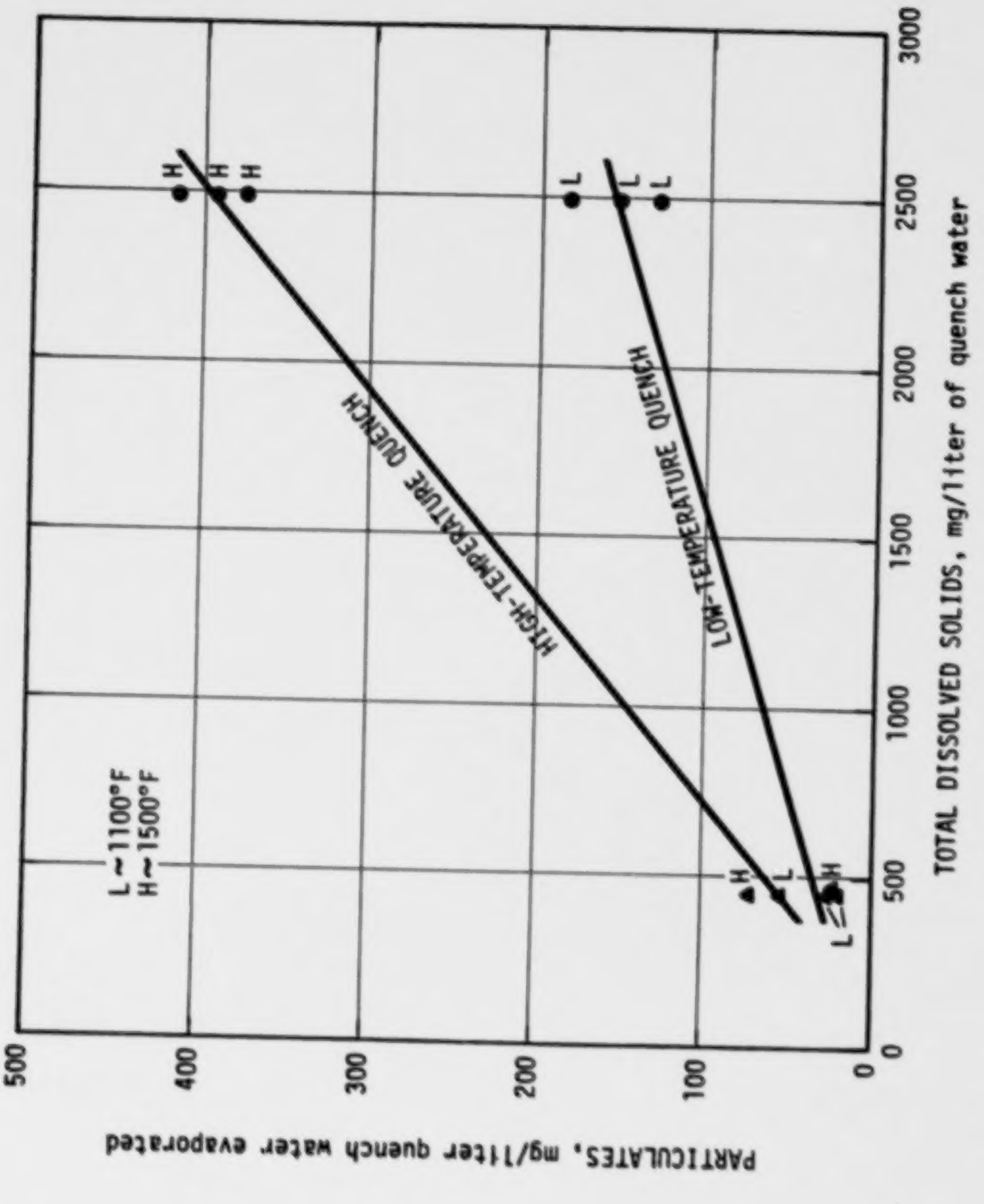


Figure 3. Particulate emissions vs. total dissolved solids in quench water.

(TDS = 450 mg/liter) and 613 mg per liter for BF blowdown water (TDS = 2491 mg/liter), respectively. These values are compared with those calculated from coke quenching tests in Table 4. It is projected that under roughly comparable conditions of temperature and TDS levels, slag quenching produces significantly lower emissions.

TABLE 4. PARTICULATE EMISSIONS DURING COKE QUENCHING AND SLAG QUENCHING

	Coke quenching		Slag quenching	
	Low TDS water	High TDS water	Low TDS water	High TDS water
TDS (mg/liter)	510	2270	450	2491
Emissions (mg per liter of water evaporated)	1184	1813	75	613

A comparison of these values with those for coke quenched with clean and dirty water (comparable TDS) seems to indicate that hard slag quenching with mill service water and BF blowdown water produces considerably fewer particulate emissions. No firm conclusions can be drawn, however, until data on slag quenching emissions from actual production facilities are available to establish the validity of the linear particulate-TDS relationship and the absolute emission levels.

One possible explanation for higher particulate emissions from coke quenching as opposed to BF slag quenching is that coke is more porous than slag and a larger surface area is exposed to the quench water than with slag, where only the top surface of the slag is exposed in the pit. Also the formation of steam during quenching, with its explosive shattering effect, is more pronounced in coke quenching than in slag quenching. The emissions generated from the TDS in the quench water is superimposed over the particulates generated by the explosive shattering effect in both coke quenching and slag quenching.

Based on this experimental data, an emission factor for slag quenching with BF blowdown water (TDS ≈2500 mg/liter) at two slag temperature ranges was calculated for hard slag quenching.

Low-temperature slag quench: (14.5 gal of quench water evaporated per ton of hot metal and a slag volume of 660 lb/ton of hot metal)	0.02 lb/ton of hot metal
High-temperature slag quench: (12.47 gal of quench water evaporated per ton of hot metal and a slag volume of 660 lb/ton of hot metal)	0.04 lb/ton of hot metal

The particulate emissions generated by high-temperature slag quench with blast furnace blowdown water (0.04 lb/ton of hot metal) are significantly lower when compared with uncontrolled blast furnace casthouse emissions (0.6 lb/ton of hot metal) (4).

Hydrogen Sulfide, Sulfur Dioxide, Hydrogen Cyanide, Ammonia, and Fluorides

Tables 5 through 9 show results of the air samples collected. The units in the last column for each pollutant are expressed as mg/liter of quench water applied.

TABLE 5. HYDROGEN SULFIDE (H_2S) EMISSIONS

Type of water	Slag temperature, °F	Slag sulfur content, %	Slag basicity	H_2S, mg/liter
Mill service water	1142	1.29	1.130	23.2
Mill service water	1428	1.01	0.880	Not detected
BF blowdown water	1117	1.20	1.102	5.9
BF blowdown water	1411	1.21	1.078	0.1

Several previous studies have been conducted regarding H_2S emissions during BF slag quenching. The exact mechanism of H_2S emissions is not well understood. The H_2S data generated during these tests are inconclusive.

TABLE 6. SULFUR DIOXIDE (SO_2) EMISSIONS

Type of water	Slag temperature, °F	Slag sulfur content, %	SO_2, mg/liter
Mill service water	1120	1.30	165
Mill service water	1523	1.01	360
BF blowdown water	1116	1.25	350
BF blowdown water	1633	1.22	164

The SO_2 content does not show any relationship to water quality, slag sulfur content, or quench temperature.

TABLE 7. HYDROGEN CYANIDE (HCN) EMISSIONS

Type of water	Slag temperature, °F	Total cyanides in water, mg/liter	HCN, mg/liter
Mill service water	816	0.03	<0.0057
Mill service water	1443	0.03	<0.012
BF blowdown water	1059	0.12	0.0027
BF blowdown water	1763	0.12	0.0008

The HCN data show a possible breakdown of cyanide both at low- and high-temperature slag quench.

TABLE 8. AMMONIA EMISSIONS

Type of water	Slag temperature, °F	Ammonia in water, mg/liter	Ammonia, mg/liter
Mill service water	1040	<0.2	1.4
Mill service water	1443	<0.2	3.5
BF blowdown water	1099	33.3	33.6
BF blowdown water	1472	33.3	10.1

When blast furnace blowdown water is used, the ammonia appears to break down at higher quench temperatures. Also the ammonia emissions are higher if the quench water contained higher ammonia concentration.

TABLE 9. FLUORIDE EMISSIONS

Type of water	Slag temperature, °F	Fluorides in water, mg/liter	Fluorides, mg/liter
Mill service water	816	1.84	35.3
Mill service water	1443	1.84	238
BF blowdown water	1059	15.1	32.4
BF blowdown water	1476	15.1	157

The fluorides generation does not show any trend with concentration in quench water or the quench temperature.

Hydrocarbons: C_1 to C_7 and C_7 to C_{16}

Grab samples of air emissions were taken from each test run and analyzed for hydrocarbons C_1 through C_7. In a few cases, methane was detected in the range of 1.2 to 23.7 ppm; in the rest, it was below the detection limit of 1 ppm. The presence of C_2 through C_7 was generally undetectable or at very minor levels.

Total organics in the air samples (C_7 through C_{16}) collected in the SASS train do not show any relationship to either quench water type or slag temperature.

Metals

The data for 40 elements were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICAP) for different test conditions. The highest emission rates were found for aluminum, calcium, potassium, sodium, silicon, magnesium, uranium, and boron. In general, the tendency is toward higher emissions with higher slag temperatures, which is in line with particulate emissions. The metals arsenic, selenium, and mercury were also determined separately. Although present in all samples, they did not show any relationship to slag temperature or water type used during quenching.

Organics

Only one priority pollutant (3.2 mg/liter of phenol in the blast furnace blowdown water) was detected in the quench water samples. Selected runs, however, showed the presence of the following in the air emissions:

2-Chlorophenol	4 out of 5 samples
2,4-Dimethylphenol	2 out of 5 samples
Phenol	5 out of 5 samples
Fluoranthene	3 out of 5 samples
Naphthalene	4 out of 5 samples
Bis(2-ethylhexyl) phthalate	5 out of 5 samples
Butylbenzyl phthalate	5 out of 5 samples
Di-n-butylphthalate	5 out of 5 samples
Diethyl phthalate	3 out of 5 samples
Acenaphthylene	3 out of 5 samples
Anthracene and/or phenanthrene	4 out of 5 samples
Fluorene	3 out of 5 samples
Pyrene	4 out of 5 samples

The levels for phenol, 2-chlorophenol, 2,4-dimethylphenol, and phthalates were relatively high compared with other organic substances, and they bear no relationship to quench water quality or slag temperature. The following are some of the possible explanations for the presence of organics in the air samples. The formation of organics may result from slag-water reactions at high temperature in an oxygen-deficient atmosphere. It is not uncommon for some unburnt coke to be present in slag, which might contribute the required carbon. Also, minute quantities of organics present in the quench water below detection limits might have shown up in the air samples. The presence of phthalates is presumably due to binders present in the sampling train filter.

SLAG TOXICITY DATA

Eight metals tested for EP toxicity under each quenching condition were all well below allowable concentrations. The reactivity tests for cyanide all showed negative results; however, three of the four sulfide reactivity tests showed positive results.

CONCLUSIONS

The laboratory-scale assessment of simulated blast furnace slag quenching with the use of mill service water versus the use of blast furnace blowdown water produced the following major findings and conclusions:

1) The level of particulate emissions is higher when the blowdown water (with a high total dissolved solids content) is used for quenching, and the level of these emissions increases greatly when

the temperature of the slag quenched is high. The proportional increase at high temperatures is not nearly as great when mill service water is used.

2) Particulate emissions resulting from slag quenching with blast furnace blowdown water are much lower than those produced by coke quenching with semidirty water with a similar total dissolved solids content.

3) Based on this laboratory-scale evaluation, the particulate emissions generated by high-temperature slag quenching with blast furnace blowdown water are significantly lower than uncontrolled blast furnace casthouse emissions.

4) Emissions of metals increase with high-temperature slag quenching.

5) There is no EP toxicity connected with slag quenching, either with clean or blast furnace blowdown water.

6) No specific relationship was found between organic pollutants and the use of blowdown water or slag temperature during quenching.

7) No correlation was found between quench water quality or slag temperature and emissions of SO_2, ammonia, and fluoride. Cyanides appear to break down at both low- and high-temperature slag quench.

RECOMMENDATIONS

1. For better understanding of the behavior of organic pollutants during quenching, it is recommended that similar tests be carried out with spiked quench water samples.

2. Laboratory scale tests similar to the ones conducted under this project are recommended for the use of coke plant wastewater as a quenching medium for BF slag quenching.

3. To verify the test data and findings of this project, it is recommended that tests be conducted at a suitable plant site that practices hard slag quenching with mill water, blast furnace blowdown water, and if possible, coke plant wastewater.

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(3) Bloom, B. and Jeffrey, J. D. Review of coke plant quench tower particulate emission rates. In: Proceedings of the Speciality Conference of Air Pollution Control Association. Chicago, April 1981.

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METRIC EQUIVALENTS

Nonmetric units have been used for this paper for convenience. To convert to the metric system, please use the following equivalents:

Nonmetric	Multiplied by	Yields metric
°F	(°F-32)/1.8	°C
gal.	0.00379	m^3
hp	746.0	W
in.	2.54	cm
lb	0.454	kg
ton	907.0	kg

ELECTRIC FURNACE FUME GREEN BALL RECYCLING - A TECHNICAL AND ECONOMIC EVALUATION

by

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ABSTRACT

The results of electric furnace melting (EFM) fume green ball recycling tests at a carbon steel electric furnace plant are documented. Approximately 236 tons of EFM fume recovered in the primary baghouse was pelletized and charged to 52 heats during a one-week period. The effect of EFM fume green ball recycling on furnace operation, flux addition, bath and slag chemistry, fume build-up, zinc occurrence and shop area environment are evaluated. The EFM fume pelletizing and green ball stability problems, including methods for minimizing the disintegration of green balls prior to charging, are also described. An estimate of the energy and materials conservation effect and the economics of EFM fume recycling are provided.

INTRODUCTION

In 1968, Bethlehem Steel started up the electric furnace facility at its Steelton, PA plant. Presently, three electric furnaces are in operation producing about 1.25 million tpy of carbon steel which is used in the manufacture of rail and bar products. Each of the furnaces has a nominal capacity of about 170 tons per heat utilizing a wide variety of steel scrap charges in a single heat. The electric furnace operation at Steelton results in the generation of approximately 70 tpd of fume or about 40 pounds of fume per ton of steel; the fume analyzes about 20% zinc and 3% lead. Because of the high cost of disposal of the fume, methods for utilizing the fume, such as green ball recycling were investigated. Several full-scale plant tests were run at the Steelton plant to determine the feasibility of recycling the zinc-bearing fume as green balls to the electric furnaces. The implementation of this process could reduce or eliminate the need for costly handling and disposal of the fume in secured landfills, utilize contained iron and lime values in steelmaking, and increase the zinc and lead to a point where the fume would have a higher value for recovery by a zinc processor.

EFM FUME GREEN BALLING STUDY

FUME COLLECTION

The fume produced during the electric furnace operation at Steelton is vented with the off-gases through a duct in the furnace roof (No. 4 hole) and recovered in a primary baghouse (No. 1). The dust connection at the furnace roof is not continuous but is facilitated by means of a retractable segment which swings into position between the furnace roof outlet and the inlet to the duct network and, consequently, considerable mixing of furnace gas with outside air takes place. The gas flow goes through a water spray quenching tower ahead of the No. 1 baghouse. The shop area fugitive dust is collected in a separate baghouse referred to as No. 2 baghouse; the approximate ratio of fume collected by the No. 1 and No. 2 baghouses is about 10 to 1 or 65 tpd No. 1 and 5 tpd No. 2. Both of these products are pelletized for disposal and/or zinc recovery processing.

EFM FUME GREEN BALLING

To evaluate EFM fume green ball recycling at Steelton, the No. 1 baghouse fume was used. Because of logistics and the relative small quantity, the No. 2 baghouse fume was not used for the recycle tests. To implement the recycling tests two problems had to be overcome: (1) green ball deterioration, and (2) a lack of suitable green ball handling and charging facilities.

Green Ball Stability

The fume generated at Steelton contains about 10% free lime, see Table 1, and because of this relatively high lime content, the resulting hydration reaction produced during the balling operation causes the green balls to swell and eventually disintegrate. The free moisture of the green ball which acts as a binder is chemically tied up, resulting in pellet disintegration.

TABLE 1. CHEMICAL ANALYSIS OF STEELTON EFM FUME

Chemical Analysis % dry basis	Typical	Recycled
Zn	20.0	29.8
Pb	2.7	5.6
Cd	0.05	0.08
S	0.16	0.20
Cu	0.25	0.20
Cr_{tot}	0.13	0.07
F	0.53	0.50
Cl	1.7	3.4
Fe_{tot}	24.5	15.3
CaO_{tot}	18.1	10.1
CaO_{free}	10.0	7.0
SiO_2	3.2	1.7
Na_2O	1.8	3.9
K_2O	1.3	2.0

Laboratory and plant green balling tests have demonstrated that the physical stability of the green balls is suitable for handling and charging to the electric furnaces if recycled within two hours after forming. After two hours the green balls break down and are not suitable for recycle. To improve green ball quality, it is necessary to complete the hydration reaction during the balling operation. This can be accomplished by adjusting the feed rate to the balling device to achieve an 8 to 10 minute material retention time (1). Under these conditions and with sufficient moisture addition during the balling operation, a stable product can be produced. Table 2 presents pilot data using a 1-meter disc pelletizer showing the effect of retention time and green ball stability.

TABLE 2. STEELTON EFM FUME GREEN BALLING PILOT DATA

Test No.	1	2	3	4 Replicate Production Run
Feed Rate, lb/hr	630	1000	1600	630
Retention Time, min.	10	6	4	10
Disc: Pitch Angle, deg.	41	NC	NC	NC
Rotational speed, rpm	13 1/2	NC	NC	NC
Green Ball Moisture	13	12	13	12
Green Ball Breakdown				
% -100 mesh	nil	10	15	nil
% cracked pellets	nil	~25	~50	nil

By controlling the feed rate to achieve a 10-minute retention time, the resulting green balls exhibit minimal breakdown after a 24-hour storage period.

Procedure Used to Produce and Charge Green Balls

Because of the inherent green ball stability problems, the drum type pelletizer was operated at reduced feed rates of about 4 tph resulting in a retention time of 6 to 8 minutes. The green balls, sized at 3/8 x 1 1/2 inch, were conveyed to front-end loader hoppers, transported to the furnace shop, dumped into a box normally used to charge furnace limestone in emergency situations and emptied into a loaded scrap bucket. Up to three batches of green balls (4-5 tons/batch) were produced and charged in this manner -- the batches were added to the first or second scrap buckets of individual heats and, if necessary, in the third scrap bucket of a heat. Under these conditions, the green balls produced were charged into the furnaces within two hours after forming. No problems were encountered in handling and charging the green balls, nor were any unusual furnace reactions noted. The green balls produced were charged via the scrap buckets on a 24 hr/day basis for five consecutive days.

PLANT RECYCLING DATA

FUME GENERATION RATE

The amount of green balls charged per heat averaged about 10,000 pounds for the first twelve heats at the start of the test. This amount was judged to be sufficient to consume all the fume normally produced plus an anticipated build-up of fume because of increased loading of volatiles (Zn, Pb, alkalies). The fume build-up did not occur and it was possible to reduce the green ball charge and consume all the collected fume. As a result, the amount of green balls charged was reduced to 8/9000 pounds per heat; the thirteen subsequent heats had less than 8000 pounds charged. During the five day test period, the overall average charge was 9100 pounds; however, actual fume generation levelled off at about 7000 lb per heat or 2% by weight, comparable to normal production rates without green ball recycling.

EFFECT OF GREEN BALL RECYCLING ON FURNACE OPERATION

Production data were examined to determine the effect of green ball recycling on power consumption, heat time and flux addition. The data were averaged according to four levels of green balls charged, see Table 3. From this evaluation, and comparing these averages with yearly plant averages, an apparent increase in power consumption occurred, while no effect in heat time was apparent. Flux addition, i.e., limestone, lime and fluorspar, showed a slight increase.

TABLE 3. SUMMARY OF OPERATING DATA FOR EFM FUME GREEN BALL RECYCLING

No. of Heats	Amount of Green Balls Charged, lbs	Heat Time min.	Power kwh/ingot ton	Fluxes (lb/ingot ton) Lime	Stone	Spar
2	<6,000	160	483	29	65	0.0
32	6,000/ 9,000	190	517	48	73	1.2
15	10,000/12,000	187	538	67	96	1.0
3	+12,000	191	546	53	71	0.3
Yearly Avg.		190	482	31	94	1.3

Effect of Green Ball Recycling on Power and Heat Time

To statistically quantify the effect of green ball recycling on the power consumption and heat time, the plant data were plotted using a computer interpretation based on delta weighing factors. Figure 1 shows a plot of the power consumption in kwh/ingot ton as a function of green ball addition. The curve generated shows a gradual increase in power for green balls charged. A second power curve is shown derived from a computer program developed in connection with a DOC funded Lehigh University study (2) which estimates the energy consumption for recycling EFM fume green balls, based on: evaporation of water, calcination of fluxes, vaporization of volatiles, etc. The power curves, actual and theoretical, are essentially the same, and can be used to predict power consumption for EFM fume green ball recycling.

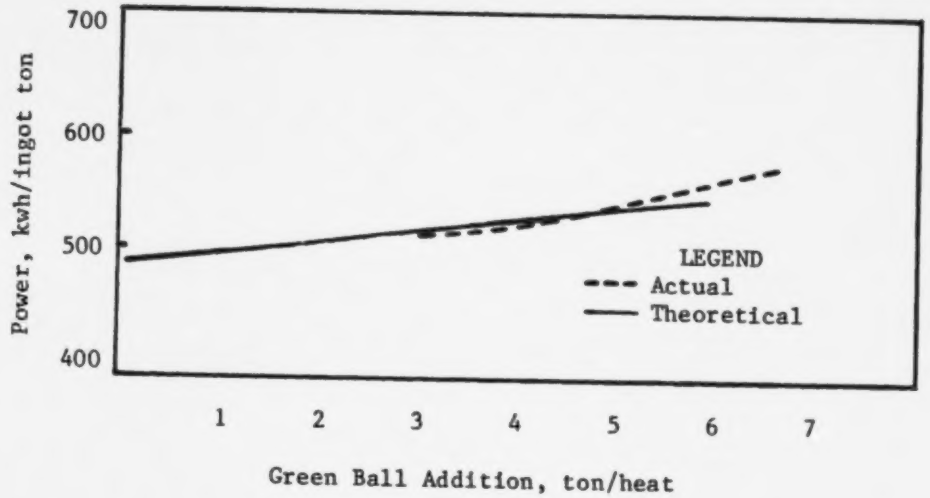

Figure 1. Power Consumption as a Function of Green Ball Addition.

Using the computer program, the following are the calculated power consumptions expressed as a percent increase per green ball charge:

Green ball addition, ton/heat	Net power increase, %
2	1.7
3	5.4
4	7.5
5	9.2
6	11.0

The projected heat time, tap to tap, for green ball recycling is graphically depicted in Figure 2, using the computer plotting technique. The curve generated shows essentially no change in heat time for green balls charged, up to about 12,000 pounds. The average heat time was the same as the yearly average for the plant, about 190 minutes. Little or no extension of heat time occurred as a result of green ball recycling within the range tested.

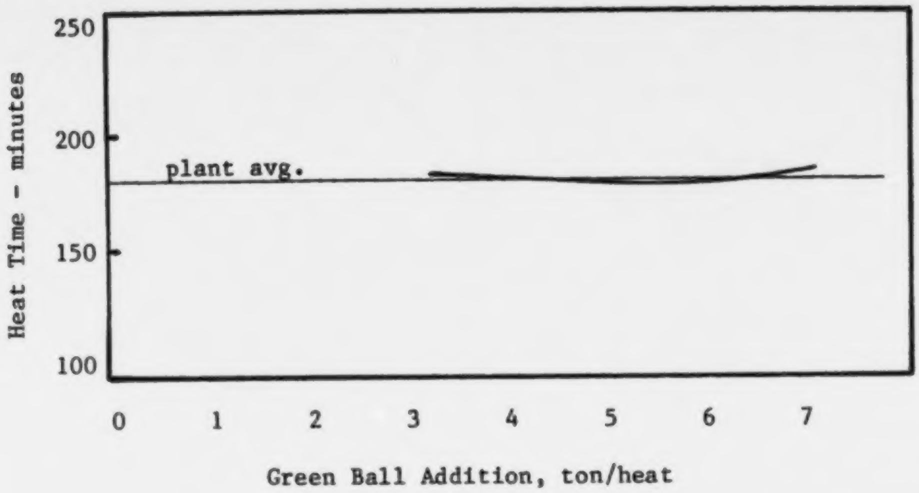

Figure 2. Electric Furnace Heat Time Versus Green Ball Addition.

Effect of Green Ball Recycling on Bath Chemistry

Charging green balls affected the carbon content of the bath on the first test analysis. This was particularly evident for the early heats in the trial when 10,000 pounds or more were charged. Plant operating personnel decided to increase the amount of scrap iron to the heats by approximately 20,000 pounds to prevent low carbon melts. Table 4 summarizes plant operating data showing the effect of green balls on bath carbon.

TABLE 4. EFFECT OF EFM FUME GREEN BALL RECYCLING ON BATH CARBON

Aim Carbon	No. of Heats	Pounds of Scrap Iron Charged x 1000	Pounds of Pellets Charged	First C Test
.73/.79 C, Rail	6	70 - 75	0	.81
"	8	90 - 100	4,000 - 9,600	.94
"	7	90 - 95	10,000 or more	.75
.44/.46 C, Bar	1	6 - 8	0	.46
"	3	20 - 29	~10,000	.49
"	7	20 - 26	10,000 or more	.33

The extra carbon provided by the iron was needed to compensate for the oxides in the green balls. For example, if the amount of green balls is limited to 6000 to 8000 pounds per heat, approximately 20,000 pounds of additional iron in the charge is required.

The melt sulfur increased during the recycling test exceeding the 0.05% S limit, necessitating flux changes, see Table 3; however, overall the amount of fluxstone charged during the test did not significantly differ from normal flux addition. No other changes occurred with bath chemistry as a result of recycling.

Effect of Green Ball Recycling on Zinc Occurrence

The total zinc content of the fume increased from the normal 20% Zn to about 35% Zn after about 24 hours into the test, but then decreased to about 30% Zn, see Figure 3. Based on these data and the type of scrap being charged, the equilibrium level for green ball recycling at Steelton was about 30% Zn.

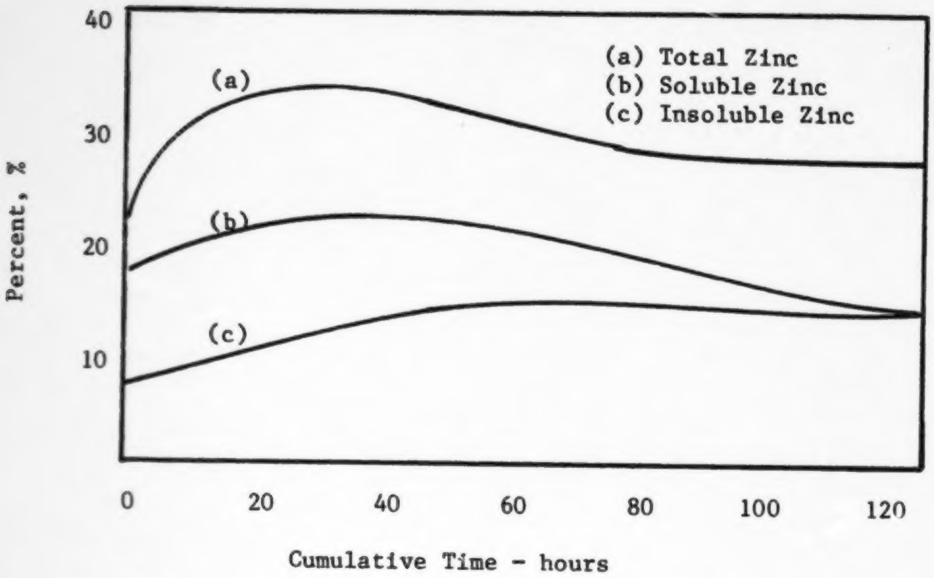

Figure 3. Zinc Content of Recycled Green Balls as a Function of Time

Included in Figure 3 are curves showing the soluble and insoluble zinc content of the recycled EFM fume green balls. These data were obtained from Muspratt leach tests run on the green ball samples. The soluble zinc content followed a similar trend as the total zinc, increasing from about 16% sol. Zn to about 25% sol. Zn and then decreasing and leveling off at the initial level of 16%. Conversely, the insoluble zinc increased with time but did level off at about 15%. Complete chemical analysis of the recycled fume are listed in Table 1, which also includes analysis of typical Steelton EFM fume.

Analyses of slag samples were conducted to determine if recycling had has any affect on slag chemistry. Approximately 6 tons of EFM fume green balls were added to a test heat. During this test both the entire flush and tap slags were collected and sampled. A base test without green balls was also sampled for comparison. Chemical analysis of the slag samples, see Table 5, showed no appreciable levels of volatiles in the various slag samples.

TABLE 5. CHEMICAL ANALYSIS OF STEELTON SLAG (TAP AND FLUSH)

Green Ball Charge, lb	0		12,200	
Chemical Analysis, %	Flush	Tap	Flush	Tap
SiO_2	19.7	20.7	19.0	20.4
Al_2O_3	7.6	8.1	7.2	7.6
CaO	40.3	41.6	43.9	43.4
MgO	7.5	7.2	6.6	7.1
Fe_{tot}	26.1	21.0	23.6	20.6
Fe^{o}	14.7	11.8	13.3	11.6
Tot. Alkali	1.1	1.0	1.0	1.0
Zn	< .05	< .05	< .05	< .05
Pb	< .05	< .05	< .05	< .05
Cd	< .05	< .05	< .05	< .05

During these single heat tests, the shop area environment was also sampled by plant environmental personnel. They reported that during the green ball recycling tests, the shop area actually exhibited lower concentrations of the zinc and other particulates than during the base test without green ball recycling.

COMPUTER STUDY TO ESTIMATE THE ENERGY AND MATERIALS CONSERVATION EFFECT AND THEIR APPROXIMATE ECONOMIC BALANCE

The computer program used for evaluation of power consumption for green ball recycling, see Figure 1, was also used to compute the economics for green ball recycling. This program was run using Steelton costs (power, etc.), operating data, and a green ball recycle rate of 3.5 tons per heat. The projected cost for recycling amounts to about $0.70 per ton of steel. This program, however, did not account for the added cost for additional iron to achieve the carbon specifications. Our analysis indicates that the increased iron, such as molds, stools, etc., would incur an additional cost of $0.12 to $0.20 per ton of steel for the incremental iron required, see Table 6.

TABLE 6. RECYCLING ELECTRIC FURNACE FUME - APPROXIMATE OPERATING COSTS

	$/Ton Steel
Recycling Fume	
Debit	
- Extra Power Cost	1.04
- Extra Iron Charged to Maintain Carbon Spec.[1]	0.12 to 0.20
Subtotal	1.16 to 1.24
Credit	
- Conservation of Fe Units	0.31
- Conservation of CaO Units	0.04
Subtotal	0.35
Total Cost	0.81 to 0.89

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[1] Other methods for adjusting bath carbon might be used which could affect costs.

CONCLUSION

A one-week EFM fume green ball recycling plant test was conducted at a carbon steel electric furnace shop to learn more about this process as a potential means for disposing of the fume. Extensive testing and sampling was performed prior to, during, and after the test to develop reliable green balling and charging techniques, and to determine what affect recycling has on furnace operation. Some of the pertinent information developed from this study included: (1) green ball stability is improved by increasing material retention time to about 8 minutes during the agglomeration step, (2) recycling does not affect slag chemistry but does lower the bath carbon content, (3) fume generation does not increase over normal levels but is enriched resulting in a 30% zinc content (20% Zn normal), and (4) recycling does not increase heat time but will increase power consumption. Computer programs which were developed for estimating the energy and materials conservation effects for recycling EFM fume, have been verified from this testing and can be used to estimate the approximate operating costs for EFM fume green ball recycling to carbon steel furnaces.

Overall, the plant test has demonstrated that green ball recycling can be used as a means for disposing EFM fume but that recycling will increase furnace operating costs. Depending upon the plant conditions, the costs could be offset by eliminating disposal costs.

ACKNOWLEDGMENTS

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APPLICATION OF ARMCO FIXATION TECHNOLOGY ON OPEN HEARTH WET SCRUBBER SLUDGE

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ABSTRACT

With the advent of RCRA, Armco's Middletown Works Open Hearth Wet Scrubber sludge failed the Extraction Procedure (EP) Toxicity Test for lead and cadmium. This material was initially disposed of in an approved hazardous waste landfill at enormous transportation and disposal costs while ongoing investigations were conducted to detoxify this waste. Several solidification/fixation processes were evaluated, including one developed by Armco. The Armco phosphate fixation process proved to be the most cost efficient because of the low capital and operating costs associated with it and the ease of installation at an existing facility. The process has been successfully applied at full-scale to the Open Hearth System. The concentrations of lead and cadmium in the leachate have consistently been well below EP toxicity limits. The state environmental agency has allowed the plant to landfill the treated waste at their existing solid waste site. The capital and operating costs for full-scale treatment are described and compared to the initial hazardous waste landfill costs. The operating problems experienced with phosphate fixation technology on the air pollution and water pollution equipment are described.

INTRODUCTION

In recent years, the steel industry has been faced with rising operating costs associated with treatment, storage, and disposal of hazardous wastes as a result of the Resource Conservation & Recovery Act (RCRA). The steel industry has typically generated large volumes of inorganic wastes in both dry and semi-liquid or sludge forms which are low in toxicity when compared to other industrial wastes. Generally, hazardous wastes generated by the steel industry are designated as toxic because of leachable metals contained in them. For example, the two major listed wastes in the steel industry - electric arc furnace (K061) dust and spent pickle liquor (K062) - are considered toxic because of chromium and lead. Many steel companies also operate processes related to steel making and finishing such as electroplating operations. Hazardous wastes generated from these operations are also considered toxic because of heavy metals which include cadmium, chromium, and nickel. Other operations within the steel industry may generate solid, inorganic wastes that are hazardous due to failing the EP toxicity characteristic test for metals.

Armco has recently developed a patent-pending process which can fix or stabilize heavy metals contained in wastes from processes such as these to render the wastes non-hazardous. The process has been successfully applied to hazardous waste from an Open Hearth Shop. This report describes the Armco process and its application on Open Hearth hazardous wet scrubber sludge which has resulted in savings of $60/ton (wet dewatered sludge).

ARMCO'S PHOSPHATE FIXATION PROCESS

Armco's process uses various forms of phosphates to fix or stabilize heavy metals. The phosphates are believed to form very stable heavy metal precipitates.(1) The reaction converts dissolved metals and less stable metal hydroxides and oxides to the more stable phosphate form. The phosphate precipitate is not significantly soluble between pH of 2 to 12. It appears to form very rapidly. The process can be applied to dusts, clarifier underflow slurries, or dewatered sludges.

Since the process does not attempt to solidify the waste, it has several advantages over most commercial processes.(2) They are as follow:

1. There is no chemical demand by free water contained in the sludge. Consequently, the process can be applied to clarifier underflow slurries. This eliminates extensive sludge handling, mixing, and chemical storage equipment.

2. There is no noticeable increase in sludge volume.

3. There is no change in dewatered sludge consistency.

Several bench scale studies have been conducted at Armco's Research Laboratory to evaluate the effectiveness of the phosphate process when applied to steel making sludges. The data from these studies have shown substantial reduction in the heavy metal leachate analyses after treatment. Armco is currently in the process of obtaining leachate test data for lime neutralized sludges, electroplating sludges, and dry electric furnace dust. The phosphate fixation process has been successfully applied at full scale to Armco's Middletown Works No. 2 Open Hearth Shop. The case history is discussed below.

APPLICATION OF ARMCO'S PHOSPHATE FIXATION TECHNOLOGY

DESCRIPTION OF NO. 2 OPEN HEARTH SHOP AND ASSOCIATED POLLUTION CONTROL EQUIPMENT

Armco's Phosphate Fixation Technology has been applied to the hazardous waste sludge generated from a wet scrubber/wastewater treatment plant at an Open Hearth Shop.

A brief description of the shop and the associated air and water pollution control equipment is as follows:

Armco's Middletown Works No. 2 Open Hearth Shop was installed in the mid-1950's. It is equipped with six 300 ton furnaces, each with a maximum firing rate of 170 MMBTU/hr. The furnaces were designed to be fueled by 75% natural gas and 25% tar; however, they are fired with tar or fuel oil when natural gas is not available. The furnaces are typically operated with 100% cold charge. The cold charges contain high percentages of plant-generated coated scrap and No. 2 bundles (containing coated scrap). Heats are approximately twelve hours long tap-to-tap time.

Individual high energy wet scrubbers were installed on each furnace in 1970. Each system consists of a venturi scrubber with a flooded disc, flooded elbow, cyclonic separator, fan, and sound-attenuated stack as shown in Figure 1.

Within each scrubber system, water is recirculated to the flooded disc from a pump tank at a rate of 1000 gpm. Approximately 100 gpm per scrubber is evaporated and 400 gpm per scrubber is returned to the wastewater treatment plant for neutralization and clarification. The clarified water is then recirculated to each scrubber at a rate of 500 gpm to the wetted inlet section of the scrubber.

The wastewater treatment plant consists of primary and secondary treatment. In the primary system, the total scrubber return water at 2400 gpm is discharged into a distribution box where caustic soda is added to raise the pH of the system to 5.5 to 6 for corrosion prevention. Make-up water from the BOF Shop wet scrubber system can also be added here. The neutralized wastewater then passes through two 55 foot diameter clarifiers in parallel for solids settling. The clarified water with make-up addition is then returned to the wet scrubbers as previously mentioned at a rate of 3000 gpm. The clarifier underflow slurry is pumped to the filter building where it is dewatered on continuous belt vacuum filters.

Occasionally, it is necessary to control the build-up of dissolved solids in the primary system. Consequently, a portion of the scrubber supply water is intercepted and conveyed to the secondary system at a flow of 150 gpm. This water is further neutralized with hydrated lime to pH 8.5 and then discharged to a 35 foot diameter clarifier for solids settling. The clarified effluent is discharged to a receiving stream. The clarifier underflow slurry is also pumped to vacuum filters for sludge dewatering purposes.

The primary clarifier underflow slurry typically contains 30 to 40% solids, while the solids range 4 to 7% in the secondary clarifier underflow. With a typical four-furnace operation, approximately 32 tons per day of dewatered primary sludge are generated and 7 tons per day of secondary dewatered sludge. Both sludges contain lead and cadmium. Coated scrap is the primary source of these metals. Both sludges failed EP Toxicity for lead and cadmium; however, phosphate fixation has been applied to the primary sludge only.

CHARACTERIZATION OF DEWATERED PRIMARY SLUDGE

Historical primary sludge compositional analyses on a dry basis are shown in Table 1. This sludge is composed primarily of iron and zinc with minor concentrations of calcium, magnesium, fluoride, silicon, and lead. The concentration of cadmium is extremely low, averaging only 0.02% of the dried sludge. The moisture content of the wet dewatered sludge averages 40%.

Historical EP Toxicity leachate analyses of primary sludge are shown in Table 2 and compared to the RCRA limits. With the exception of lead and cadmium, the leachate analyses show compliance with the other EP Toxicity parameters.

Lead has routinely failed the EP Toxicity Test. Lead concentrations in the leachate have averaged 17.5 mg/l with a maximum of 48 mg/l. Cadmium has frequently failed the EP Toxicity Test. Cadmium concentrations in the leachate have averaged 0.72 mg/l with a maximum of 3.16 mg/l.

X-ray diffraction and electron microprobe analyses suggest the lead and cadmium exist in two forms in the open hearth dust. Part of each metal is in the form of oxides or hydroxides, while the remainder is tied up in an iron oxide spinel. Only the metal oxides appear to react with phosphates to form insoluble metal phosphates. The metals that make up the iron oxide spinel are relatively non-soluble.(3)(4)

TREATMENT OF OPEN HEARTH PRIMARY SLUDGE

Full Scale Trials

A full scale trial was conducted for approximately one week to evaluate the process on Open Hearth primary sludge. Phosphoric acid was selected as the form of phosphate to be used since minimal equipment was needed for adding it to the primary clarifier underflow slurries and because it was the cheapest form available. It was also compatible with the materials of construction at the Open Hearth air and water pollution control equipment. That equipment is constructed of fiberglass reinforced plastic or 316 ELC stainless steel. Metering pumps and rubber hoses were acquired for adding phosphoric acid. The metering pumps used were piston-type with double diaphragm ends. The phosphoric acid was pumped from fifty-five gallon drums to the suction side of the clarifier underflow pumps as shown in Figure 2. The mixing time between the point of acid addition and discharge of the combined underflow into the vacuum filter tank was approximately 4 minutes. There was an additional retention time in the vacuum filter tank of 16 minutes. The metering pumps were manually started whenever the slurry pumps were in operation.

During the trials, grab samples were periodically taken as the dewatered sludge dropped from the filter belt onto a conveyor. The samples were later composited prior to analyses. The results of the EP Toxicity Tests are shown in Table 3.

The concentration of lead in the leachate from the untreated sludge ranged from 3.9 to 29 mg/l and averaged 16.7 mg/l during the trials. After treatment with phosphoric acid, the concentration of lead in the leachate ranged from 0.14 to 0.76 mg/l and averaged 0.32 mg/l over the five days of sampling.

The concentration of cadmium in the leachate from the untreated sludge ranged from 0.22 to 0.62 mg/l and averaged 0.43 mg/l. After treatment, the concentration of cadmium in the leachate ranged from 0.06 to 0.14 mg/l and averaged 0.09 mg/l. Although the cadmium concentrations in the leachate of the untreated samples were below the RCRA limit of 1 mg/l, there was a reduction of cadmium in the leachate after treatment.

Primary sludge compositional analyses before and after treatment with phosphoric acid is shown in Table 4. There is virtually no change in total lead and total cadmium before and after treatment. The data show an increase in the percent phosphate contained in the treated sludge (dry basis). This result agrees with Armco's premise that dissolved lead and cadmium and oxides of lead and cadmium react with phosphate to form stable metal phosphate precipitates.

The phosphate applied to the clarifier underflow during the trials ranged from 3 to 5.4 times the stoichiometric requirements for converting lead to lead phosphate. From the results of bench scale trials at least three times the stoichiometric phosphate requirement to convert total lead contained in the sludge to lead phosphate is needed. Evidently, there are competing reactions for the phosphate from other metals such as zinc, calcium, etc. Although there are fluctuations in the lead content of the open hearth dust, the applied phosphate concentration was based on three times stoichiometric phosphate requirements at 1.5% lead in the dust.

Installation & Operation of Full Scale Phosphate Fixation Process

From the success of the one week trial, a full scale system was designed and installed. Operation began in May, 1982.

The phosphoric acid addition system as shown in Figure 1 consists of a 6000 gallon bulk fiberglass reinforced plastic storage tank with an immersion heater, three piston-type metering pumps equipped with diaphragm ends, and associated piping and control equipment. The phosphoric acid storage tank was installed outside the filter building on a concrete pad surrounded by a dike where it is conveniently located for bulk tank truck unloading.

Approximately one hundred fifty feet of 316 ELC stainless steel 1/2" and 2" diameter pipe was installed to convey phosphoric acid from the bulk phosphoric acid tank to the slurry lines at a point downstream of the two clarifier underflow slurry pumps. The wetted parts of the metering pumps are made of Carpenter 20, teflon, or viton. The metering pumps are actuated by the level control system in the vacuum filter tank which also actuates the clarifier underflow pumps. Consequently, phosphoric acid is metered into the system at a set rate whenever the slurry pumps operate.

The rate of phosphoric acid addition has been established from average historical total lead concentrations in the primary sludge, the flow rate of the underflow pumps, and bench scale data. Typically, phosphoric acid is added at five times the stoichiometric requirements to convert lead to lead phosphate to allow for a margin of safety.

The total capital cost required to install this system was approximately $70,000 as shown in Table 5.

The annual operating cost associated with the phosphate fixation process for a four furnace operation is $290,000 or $30/ton of wet sludge (see Table 5). This cost can be broken down as follows: $164,000/year or $17/ton for phosphoric acid, $26,000/year or $2.75/ton for increased caustic soda usage, $97,000/year or $10/ton for transportation and disposal at Armco's solid waste disposal site, and $3000/year or $0.25/ton for miscellaneous maintenance. No additional labor costs have been experienced. The previous operating costs for transportation and disposal at an approved hazardous waste landfill averaged approximately $1,000,000/year or $90/ton. An approximate savings in current annual operating costs of $750,000 or $60/ton has been attained.

While designing the full scale system, Armco petitioned the state agency to allow for disposal of the treated sludge at Armco's on-site solid waste landfill. The state agency approved the request based on submittal of leachate analyses of the treated sludge. Armco began hauling treated Open Hearth primary sludge to its landfill in the late spring of 1982. Approximately 15,000 tons of treated primary sludge have been landfilled since state agency approval. The State has required monthly composite sampling and analyses of the treated primary sludge. The historical EP Toxicity results of this program are shown in Table 6. The monthly average lead and cadmium leachate concentrations are 0.65 mg/l and 0.13 mg/l, respectively. There have been two months over the last fifteen where the lead leachate concentration was higher than 1 mg/l. The lead concentration reached 3.4 mg/l during one of the months as a result of improper setting of the metering pump. The maximum cadmium leachate concentration of 0.35 mg/l also occurred at this time. On the other occasion, the lead concentration was 2.4 mg/l when a ball check valve failed in the metering pump.

Qualitative analyses which included x-ray diffraction and electron microprobe techniques were recently performed on treated primary sludge to determine if the lead oxide and hydroxide are converted to lead phosphate crystals as predicted. Although the lead averages approximately 1.5% in the sludge on a dry basis, only a part of the total is amenable to phosphate treatment. Apparently the lead exists as both lead oxide and as a spinel of lead/iron oxide. Only the lead oxide is capable of dissolving during the EP toxicity test and reacting with phosphates. The lead contained in the spinel should not dissolve under the acidic conditions of the EP toxicity test nor react with phosphate.(3)(4)

Four samples of dried phosphate treated primary sludges were analyzed by x-ray diffraction and electron microprobe. Fe_3O_4 (magnetite) and Fe_2O_3 (hematite) were the major crystalline phases detected. The diffraction patterns showed evidence of Zn/Fe_2O_4 spinels. Several low intensity diffraction peaks could not be identified. Lead and cadmium phosphate compounds could not be clearly detected by x-ray diffraction, but the presence of those elements were detected by electron microprobe techniques. This discovery suggests that lead and cadmium compounds formed after phosphate treatment are amorphous or microcrystalline. The percent of lead and cadmium phosphate contained in the sludge is also near the detection limit of x-ray diffraction techniques. The analyses by electron microprobe showed that lead and cadmium were present in the sample near areas surrounded by high phosphorus peaks. This discovery suggests the formation of lead and cadmium phosphate compounds. However, similar lead and cadmium peaks were also detected in areas where there was little or no phosphorus detected. The lead and cadmium detected in these areas are probably in the form of lead/cadmium/iron oxide spinels.

While Armco has not been able to conclusively prove that lead and cadmium phosphates compounds have formed, the EP toxicity data clearly indicates that the metals have been fixed after the addition of phosphates and minimal leaching of lead and cadmium has occurred.

Operating Problems Associated with Phosphate Fixation

One of the weaknesses of the system has been the control of phosphoric acid addition. In general, overfeeding of phosphoric acid has been practiced because of lack of adequate control measurements and because of variations in lead and cadmium concentrations in the clarifier slurry. Armco is currently in the process of evaluating measurement techniques such as ion selective electrodes for rapid quantification of either lead or phosphate levels in the slurry underflow or filtrate return water. Until more refined control measures are implemented, overfeeding of phosphoric acid will continue.

Some operating practices of the clarifier underflow system have been changed as a result of phosphoric acid addition. Previously, the clarifier underflow lines and pumps, when not in use, were flushed with water. With start-up of the phosphoric acid addition system, noticeable build-up of scale occurred when the clarifier underflow piping and pumps were shut down. The build-up of scale over several days eventually plugged the lines which required high pressure water blasting. The problem has been solved by continuing to recirculate water through these lines when not in use. The increased electrical costs have been very minor as a result of this new practice.

SUMMARY AND CONCLUSIONS

In summary, Armco has developed a metal fixation process which utilizes various forms of phosphate to form metal phosphate precipitates in inorganic, steel related hazardous wastes. The process has been successfully applied at full scale to open hearth hazardous wet scrubber sludge. After phosphate treatment, lead and cadmium contained in EP test leachate has been significantly reduced to levels below EP leachate limits. Consequently, a hazardous waste costing approximately $90/ton for transportation and disposal has been converted to a non-hazardous solid waste. Treatment and disposal costs have been reduced to $30/ton of wet sludge. A net savings of $60/ton of wet sludge has resulted from implementation of this process.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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(3) Nojiri, N., Tanaka, D., Sato, K., and Sakai, Y., Electrolytic Ferrite Formation System for Heavy Metal Removal, WPCF 52 pp. 1898-1906, (1980).

(4) Swope, H. G., Hazardous Wastes Discussed at International Meeting of Chemical Societies, Ind. Wastes, Sept./Oct., 1979, pp. 16-28.

TABLE 1. HISTORICAL COMPOSITIONAL ANALYSIS OF UNTREATED PRIMARY SLUDGE (DRY BASIS)

Constituent	Range %	Avg. %
Iron	49-56	50
Zinc	5.5-9.4	7.0
Fluoride	1.5-3.5	2.2
Calcium	1.2-3.0	1.9
Magnesium	0.8-3.0	1.0
Lead	0.5-3.8	1.8
Silica	0.5-1.0	0.6
Phosphate	0.3-1.0	0.5
Aluminum	0.3-0.8	0.5
Sulfate	0.1-0.65	0.3
Cadmium	0.010-0.060	0.020
Typical Moisture Content Before Drying:	33-55	40
Specific Gravity		2
Wet Bulk Density		125#/ft^3
Particle Size Distribution	80% by Weight were 1-4 um in Diameter	

TABLE 2. HISTORICAL EP TOXICITY LEACHATE ANALYSES OF UNTREATED PRIMARY SLUDGE

Constituent	Range mg/l	Avg. mg/l	RCRA Limits mg/l
Lead	3.7-48	17.5	5
Cadmium	0.15-3.16	0.72	1
Arsenic	<0.003	<0.002	5
Barium	<0.3	<0.3	100
Chromium	<0.04	<0.04	5
Mercury	<0.0002-0.0018	0.0009	0.2
Selenium	0.003-0.005	0.004	1
Silver	<0.01	<0.01	5

TABLE 4. PRIMARY SLUDGE COMPOSITIONAL RESULTS FROM FULL-SCALE TRIALS (DRY BASIS)

Date	Sample Type	Total Lead %	Total Cadmium %	Total Phosphate %
12/10/81	Untreated	1.85	0.01	0.35
12/10/81	Treated	1.65	0.01	2.35
01/11/82	Untreated	1.4	0.012	0.32
01/11/82	Treated	1.7	0.011	2.73
01/12/82	Untreated	2.0	0.011	0.41
01/12/82	Treated	2.0	0.011	1.71
01/14/82	Untreated	1.5	0.013	1.0
01/14/82	Treated	1.4	0.012	2.9
01/15/82	Untreated	1.2	0.012	0.87
01/15/82	Treated	1.2	0.011	2.31

TABLE 3. EP TOXICITY LEACHATE RESULTS FROM FULL SCALE TRIALS

Date	Sample Type	Total Lead mg/l	Total Cadmium mg/l	Total Arsenic mg/l	Total Barium mg/l	Total Chromium mg/l	Total Mercury mg/l	Total Selenium mg/l	Total Silver mg/l
12/10/81	Untreated	22	0.22	-	-	-	-	-	-
12/10/81	Treated	0.15	0.07	-	-	-	-	-	-
1/11/82	Untreated	23	0.54	0.0003	<0.3	<0.04	0.0004	0.0006	<0.01
1/11/82	Treated	0.19	0.07	0.027	<0.3	<0.04	0.0003	0.0084	<0.01
1/12/82	Untreated	29	0.37	-	-	-	-	-	-
1/12/82	Treated	0.76	0.14	-	-	-	-	-	-
1/14/82	Untreated	5.7	0.62	-	-	-	-	-	-
1/14/82	Treated	0.37	0.09	-	-	-	-	-	-
1/15/82	Untreated	3.9	0.41	0.007	<0.3	<0.04	<0.002	0.0036	<0.01
1/15/82	Treated	0.14	0.06	0.041	<0.3	<0.04	<0.002	0.013	<0.01

Note: Phosphoric Acid Applied Ranged from 3.0 to 5.4 Stoichiometric Requirements To Convert Lead to Lead Phosphate $Pb_3(PO_4)_2$

TABLE 5. ARMCO PHOSPHATE FIXATION PROCESS CAPITAL & OPERATING COSTS

I. Capital Cost for Equipment & Installation o $70,000	
II. Operating Costs	
A. Phosphoric Acid Cost o $164,000/Yr.	$17/Ton
B. Caustic Soda Cost o $26,000/Yr.	$2.75/Ton
C. New Transportation & Disposal Cost o $97,000/Yr.	$10/Ton
D. Miscellaneous Maintenance Cost o $3000/Yr.	$0.25/Ton
Total Operating Cost o $290,000/yr.	$30/Ton (Wet Dewatered Sludge)

OPERATING COST COMPARISON BETWEEN PREVIOUS AND CURRENT TREATMENT & DISPOSAL PRACTICES

Previous Operating Costs o	$1,040,000/Year	$90/Ton
Current Operating Costs o	$ 290,000/Year	$30/Ton
Net Savings	$ 750,000/Year	$60/Ton

TABLE 6. ARMCO MIDDLETOWN WORKS NO. 2 OPEN HEARTH FULL SCALE SYSTEM HISTORICAL EP TOXICITY RESULTS

	Range	Avg.
Total Lead, mg/l	<0.02 - 3.4	0.65
Total Cadmium, mg/l	0.01 - 0.35	0.13

Total Quantity of Dewatered Sludge Landfilled = 15,000 Tons

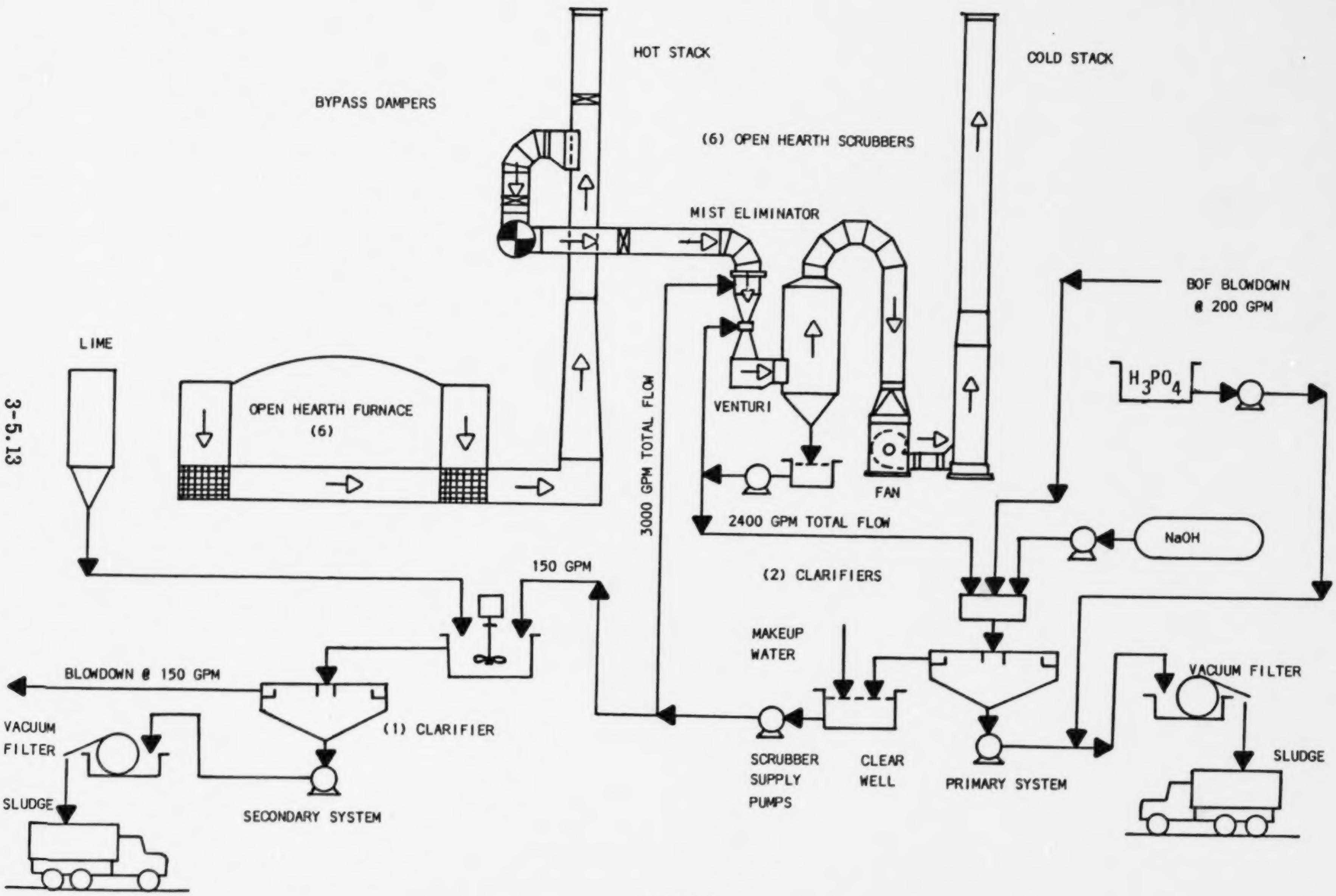
BYPASS DAMPERS
HOT STACK
COLD STACK
(6) OPEN HEARTH SCRUBBERS
MIST ELIMINATOR
BOF BLOWDOWN
@ 200 GPM
LIME
OPEN HEARTH FURNACE
(6)
H_3PO_4
VENTURI
3000 GPM TOTAL FLOW
FAN
2400 GPM TOTAL FLOW
NaOH
150 GPM
(2) CLARIFIERS
MAKEUP
WATER
BLOWDOWN @ 150 GPM
VACUUM FILTER
(1) CLARIFIER
VACUUM
FILTER
SLUDGE
SCRUBBER
SUPPLY
PUMPS
CLEAR
WELL
PRIMARY SYSTEM
SLUDGE
SECONDARY SYSTEM

FIGURE 1

ARMCO MIDDLETOWN WORKS NO. 2 OPEN HEARTH FUME CONTROL, WASTEWATER TREATMENT, AND HAZARDOUS WASTE TREATMENT SCHEMATIC DIAGRAM

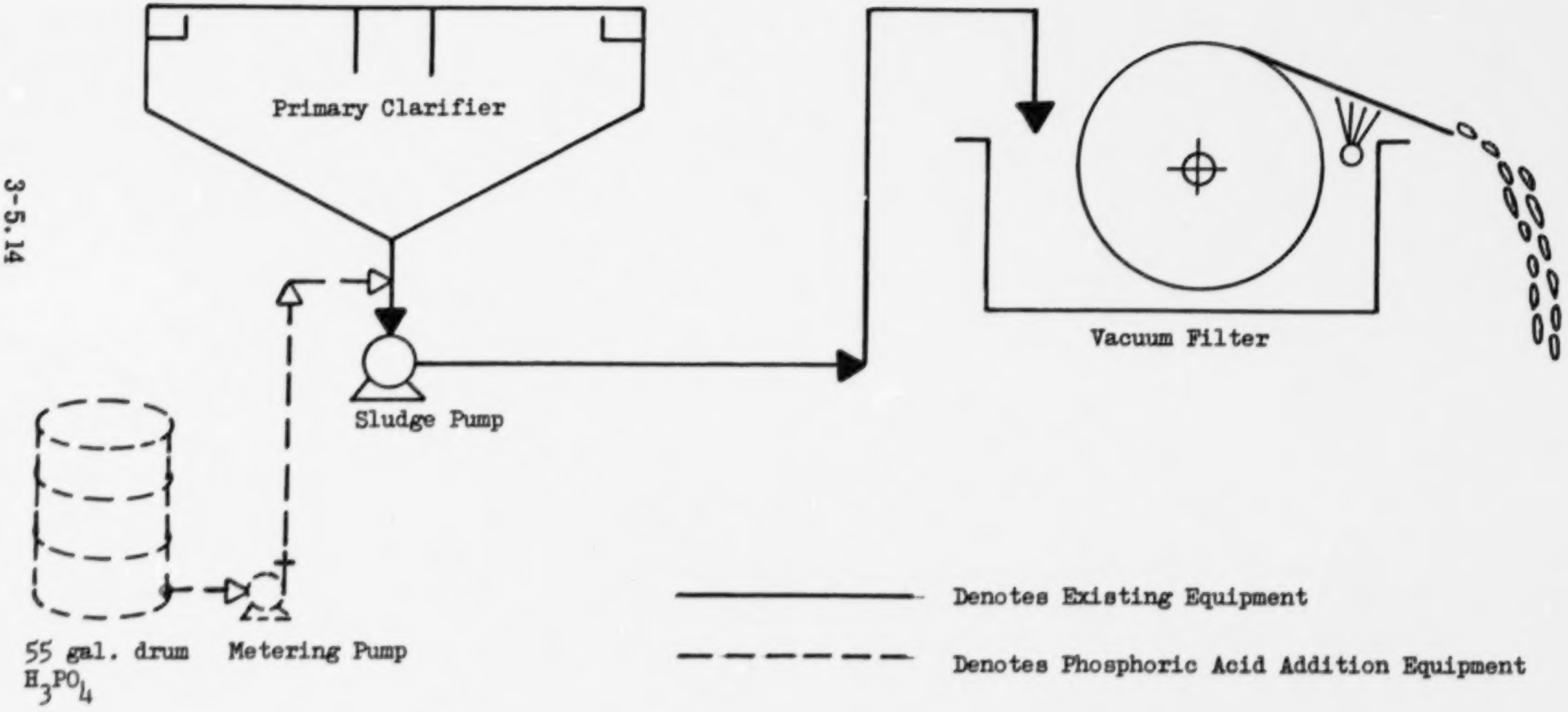
Primary Clarifier
Vacuum Filter
Sludge Pump
55 gal. drum
H_3PO_4
Metering Pump
Denotes Existing Equipment
Denotes Phosphoric Acid Addition Equipment

FIGURE 2

FULL-SCALE TRIAL AT MIDDLETOWN WORKS NO. 2 OPEN HEARTH
PHOSPHATE FIXATION WITH PHOSPHORIC ACID

CLOSURE OF HAZARDOUS WASTE STORAGE AND DISPOSAL FACILITIES AT STEEL PLANTS

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ABSTRACT

This paper will present case studies concerning closure plans and activities for hazardous waste storage and disposal facilities at two steelmaking plants. Specifically, the closure plan for active landfilling of electric arc furnace slag and dust will be examined with respect to technical approach and costing techniques. Final closure of a lagoon used to store open-hearth scrubber sludge will also be discussed.

Additionally, pertinent details of EPA guidance covering the review of closure costs will be discussed. Unit cost factors for various closure operations will be presented with respect to hazardous waste storage and disposal in the steel industry.

INTRODUCTION

The Resource Conservation and Recovery Act of 1976 (RCRA) mandated EPA to develop and enforce regulations governing "cradle-to-grave" management of hazardous wastes. This paper will focus on the "grave" aspect of the regulations, specifically as they apply to common waste management practices in the steel industry. Although the regulatory requirements are complex, and full compliance is often thought non-attainable, we hope to bring them into perspective through review of EPA guidance supplemented with an examination of two specific case studies involving closure of hazardous waste management facilities.

Closure means, in the context of the regulations, to cease waste management operations at the regulated unit (landfill, surface impoundment, etc.). Closure, or rendering an active unit inactive, can occur through normal life cycle/capacity shortfalls of the unit, or because of plant shut-down. The intent of closure is to (paraphrased from 40 CFR 264.111) control, minimize or eliminate, to the extent necessary to protect human health and the environment, post-closure escape of hazardous waste or other hazardous constituents (rainfall runoff, leachate, etc.). Depending on whether wastes are left in place or not, post-closure requirements may apply. If wastes are left in place, post-closure care must continue for 30 years after closure.

Additionally, some key definitions may be useful:

> "Active portion" means that portion of a facility where treatment, storage, or disposal operations are being or have been conducted after November 19, 1980 and which is not a closed portion.
>
> "Closed portion" means that portion of a facility which an owner or operator has closed in accordance with the approved facility closure plan and all applicable closure requirements.
>
> "Disposal facility" means a facility or part of a facility at which hazardous waste is intentionally placed into or on any land or water, and at which waste will remain after closure.
>
> "Facility" means all contiguous land, and structures, other appurtenances, and improvements on the land, used for treating, storing, or disposing of hazardous waste. A facility may consist of several treatment, storage, or disposal operational units (e.g., one or more landfills, surface impoundments, or combinations of them).
>
> "Landfill" means a disposal facility or part of a facility where hazardous waste is placed in or on land and which is not a land treatment facility, a surface impoundment, or an injection well.
>
> "Pile" means any noncontainerized accumulation of solid, nonflowing hazardous waste that is used for treatment or storage.
>
> "Surface impoundment" or "impoundment" means a facility or part of a facility which is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although it may be lined with man-made materials), which is designed to hold an accumulation of liquid wastes or wastes containing free liquids, and which is not an injection well. Examples of surface impoundments are holding, storage, settling, and aeration pits, ponds, and lagoons.

The above definitions are taken from the RCRA regulations, specifically 40 CFR 261.10. The closure and post-closure regulations can be found in 40 CFR 265.110 - 265.120 (interim status facilities) or 40 CFR 264.110 - 264.120 (finally permitted facilities). The remainder of the discussion will attempt to translate the regulations into real world applications. Hopefully, the cases selected are general enough to apply to almost any closure or post-closure effort.

CLOSURE AND POST-CLOSURE COST FACTORS

The purpose of this section is to provide a basis for estimating closure and post closure costs for hazardous waste management facilities, specifically waste piles, surface impoundments, and landfills. Ranges of costs and, where applicable, data for elements that affect cost estimates are provided. Because circumstances vary significantly among hazardous waste management sites in terms of waste quantities and types and specific procedures anticipated for closure, cost factors are presented for unit operations.

The cost data presented in this report have been derived from a variety of sources including phone surveys of companies providing specific services, construction cost estimating manuals, and U.S. EPA reports published by NTIS. Because of the large number of variables affecting closure costs, it is possible that unit operation costs may fall outside the ranges presented here.

Some of the major factors which can influence the costs are:

- The economy of scale in using large equipment and dealing with large sites versus small sites.
- The availability of clay, sand, gravel, and topsoil at or near the site.
- The surface water control measures required.

Waste Piles

Waste pile closure includes removal or decontamination of waste inventory and residues and of all containment system components, equipment, and subsoils that have been contaminated with waste and leachate. If not all contaminated portions of the pile liner or subsoils can be removed or decontaminated, the pile must be closed as a landfill. In this case the post-closure care requirements for landfills apply.

Table 1 summarizes cost data for waste pile closure procedures. Equipment costs and output are average national costs reported by construction contractors. Labor costs are based on average union labor rates and benefits for specific mixes of crews in the construction industry. The contractor profit and overhead included in contractor rates is 25 percent. In addition, contingencies of 20 percent on top of any contracted cost estimate would be considered normal.

When a pile is closed under 40 CFR 264, a drainage layer overlying the liner has to be removed at a minimum, unless the pile is closed as a landfill. The draft RCRA guidance for new waste pile design specifies that at least a twelve-inch drainage layer must overlay the pile liner. For existing waste piles the underlying materials would constitute these liner/drainage layers specified for new designs. Consequently, at least this amount of aterial must be removed at closure. The removal requirement for the liner or subsoils depends on the degree of contamination as determined from soil testing. If a synthetic liner is present and must be removed, it is necessary to first remove, in addition to the leachate collection layer, a six-inch bedding layer overlying the liner.

Waste residues on equipment and contaminated areas or structures can be cleaned by solvent cleaning, steam cleaning, sandblasting, or washing with water.

TABLE 1. COST DATA FOR WASTE PILE AND SOIL REMOVAL

Function	Approximate cost
Inventory removal with front-end loader	
4 yd^3 bucket, 280 yd^3/hr	\$0.55/yd^3
10 yd^3 bucket, 600 yd^3/hr	\$0.60/yd^3
Excavation of leachate layer and soil	
4 yd^3 bucket, 130 yd^3/hr	\$1.25/yd^3
10 yd^3 bucket, 326 yd^3/hr	\$1.15 yd^3
300 hp dozer, 150 yd^3/hr	\$1.00/yd^3
3-1/2 yd^3 crawler backhoe, 150 yd^3/hr	\$1.50/yd^3
3/4 yd^3 wheel mounted backhoe, 35 yd^3/hr	\$2.90/yd^3
Transport costs, 20 ton/truck	\$2.50-3.00/loaded mile
Disposal costs, bulk disposal at hazardous waste landfill	\$50.00-75.00/ton
Onsite hauling, contracted in 6 yd^3 to 20 yd^3 trucks, up to 1 mile round trip	\$1.30-2.30/yd^3

Contractor charges for steam cleaning and sandblasting are based on the use of three-man and four-man crews, respectively. The contract cost ranges for all three cleaning methods are:

Solvent cleaning	\$0.35 - \$4.00/ft^2 cleaned
Steam cleaning	\$0.80 - \$1.30/ft^2 cleaned
Sandblasting	\$0.60 - \$1.80/ft^2 cleaned

These costs include labor, equipment and materials. All three of the cleaning methods will produce residual materials.

Unless cleaning residuals are exempt or are shown not to exhibit hazardous characteristics, they need to be transported offsite for disposal at a hazardous waste disposal facility.

When soil is to be tested for contamination to determine if it should be removed, it is necessary to collect soil samples at varying depths. Contractor costs for auger samples range from \$6.70 to \$7.80 per linear foot, depending on the diameter of hole (2.5 and 4 inches, respectively). Cased borings range in cost from \$8.50 - \$14.50 per linear foot.

Truck transport of bulk solids up to 20 tons and bulk liquids up to 8,000 gallons was quoted in the range of \$2.50 to \$3.00 per loaded mile. A loaded mile refers to the cost per mile, one way, to the disposal facility assuming a full load. Unit costs, i.e., cost per ton, drum, or gallon of waste, will increase in direct proportion to the increase in shipping distance or to the decrease in shipping capacity utilization (less than full loads).

Onsite disposal costs should be lower than offsite disposal costs, because they do not include profit margin and capital costs that are part of offsite disposal costs. Table 1 includes expected unit trucking costs for onsite disposal. This cost assumes a one mile haul distance using plant trucking.

Landfills

Table 2 includes cost estimates for the operation and maintenance of surface water controls. The applicability of these data depends on the size and configuration (e.g., extensive use of dikes, berms, etc., and their construction) of control measures.

TABLE 2. COST OF SURFACE WATER CONTROL

Function	Approximate cost
Berm maintenance	\$0.20-0.35/yd^2 per year.
Diversion ditch maintenance	\$2.25-5.30/yd^3 per year. Assumes work on ditch twice per year after major storms.
Runoff collection, overland flow through ditches	\$37/acre/yr for sites approximately 1000 acres. \$294/acre per yr for sites approximately 10 acres. Assumes biennial cleaning of ditches.
Runoff collection, gravity pipe	\$4/acre/yr for sites approximately 1000 acres. \$49/acre per yr for sites approximately 10 acres. Includes periodic cleaning of inlets and maintenance of gravity pipe.
Pumping costs, 1 mgd	\$32,000 for 300 ft run.
Pumping costs, 10 mgd	\$280,000 for 300 ft run.

Three types of monitoring are required during the closure and post-closure periods: 1) soil-pore liquid monitoring; 2) soil core monitoring; and 3) groundwater monitoring. Soil-pore liquid monitoring and soil core monitoring in the unsaturated zone will vary among facilities, depending on the principal hazardous constituents (PHC's) designated for the wastes.

Unless the facility is exempt under provision of 40 CFR 264.90, groundwater monitoring requirements include at least semiannual sampling and analysis for groundwater contamination indicator parameters specified in the permit. Groundwater analyses for basic water quality parameters plus TOC and TOH cost about \$230/sample plus about \$60 - \$70/sample for sample collection. Soil sample analyses for contamination indicators (TOC, TOH, and specific conductance) cost about \$130/sample.

Guidance on hazardous waste land treatment recommends final grading of the treatment zone into a series of terraces to minimize erosion. If the topsoil in the treatment zone has been removed for offsite disposal it may be necessary to replace it with additional topsoil. In other cases the closure plan may show capping with a layer of clay followed with topsoil. These basic differences can be expected to produce significant variations in the costs of establishing cover at different facilities.

Additional cost differentials can be expected from the use of seeding versus sod application and differences in lime and fertilizer requirements. Approximate cost factors are given below:

Rough grading	$\$2.00/\mathrm{yd}^3$
Fine grading	$\$0.40/\mathrm{yd}^3$
Topsoil, haul 5 miles, spread	$\$9\text{-}11/\mathrm{yd}^3$
Field seed and fertilize	\$700/acre

Surface Impoundments

Two options are available for surface impoundment closure: 1) removal of all wastes, liners, and contaminated materials; and 2) removal of none or only part of the contaminated materials and disposal of the remainder onsite. If all materials are removed, no post-closure care requirements apply. If any contaminated materials remain, the post-closure requirements for landfills apply.

Sludge may be removed from the impoundment by the use of either dry techniques or wet techniques. Dry removal requires air drying of the sediment after the impoundment has been dewatered. The cost data are shown in Table 3 for conventional excavation with dozers, front-end loaders, draglines, and hydraulic dredging. Draglines are suitable for excavating very large land areas.

Closure With Wastes Remaining in Place--

If wastes are to remain within the impoundment, regulations require that the impoundment be closed as a landfill, including control of surface water and groundwater and provision of a final cover. 40 CFR 264 specifies the following for surface impoundment closure:

- Elimination of free liquids by removing liquid wastes or solidifying the remaining wastes and waste residues.

TABLE 3. COSTS FOR SLUDGE REMOVAL FROM SURFACE IMPOUNDMENTS

Function	Approximate cost
Dry removal	
Spreading, piling with front-end loader	Hourly output 45 to 185 yd^3 \$0.60 to \$1.30/yd^3
Dozer	Hourly output 50 to 150 yd^3 \$0.85 to \$1.15/yd^3
Dragline	Hourly output 35 to 65 yd^3 \$1.45 to \$2.50/yd^3
Wet removal	
Dredging	
Barge-mounted dragline or clamshell, hopper dumped, pumped 1000 ft to shore	
Minimum cost	340 yd^3/day output \$4.30 to \$5.45/yd^3
Maximum cost	245 yd^3/day output \$6.00 to \$7.60/yd^3
Hydraulic method, pumped 1000 ft	
Minimum cost	460 yd^3/day output \$3.15 to \$4.00/yd^3
Maximum cost	310 yd^3/day output \$4.70 to \$5.95/yd^3
Mobilization cost (applied to each of the above wet dredge methods)	
Minimum	\$4,500 to \$5,500/job
Maximum	\$23,700 to \$29,300/job
Backfill	
Dozer, no compaction	\$0.70 to \$0.85/yd^3
Dozer, vibrating roller	\$1.50 to \$1.75/yd^3
Dozer, sheepsfoot roller	\$1.60 to \$1.90/yd^3

- Stabilization of remaining wastes to a bearing capacity sufficient to support final cover.
- Covering the impoundment with a final cover sufficient to:
  1) Provide long-term minimization of migration of liquids through the closed impoundment.
  2) Function with a minimum of maintenance.
  3) Promote drainage and minimize erosion and abrasion of the final cover.
  4) Accommodate settling and subsidence to maintain the final cover integrity.
  5) Have a permeability less than or equal to that of any bottom liner or subsoils present.

Post-Closure requirements include:

- Maintenance of leak detection systems installed in accordance with 40 CFR 264.222 requirement for impoundments with double liners, if possible.
- Maintenance of groundwater monitoring systems.
- Prevention of erosion of the final cover by run-on and runoff.

If wastes remain in place, it is necessary to ensure that they are sufficiently consolidated and stabilized to provide long-term support for cover materials. Much of the technology for solidification and stabilization of wastes is proprietary. Many of the solidification techniques are highly waste-specific which results in a wide range of costs for stabilization. Table 4 summarizes some of the available general cost data for stabilization. It may be necessary to conduct comprehensive tests during this phase of impoundment closure to ensure that the stabilized sludge matrix will be of sufficient strength to support the cover.

The guidance for surface impoundment closure specifies that the minimum cap will include three layers: 1) low permeability lower layer, 2) middle drainage layer, and 3) vegetated top cover.

Unit operations required for constructing the lower component of the bottom layer, which consists of two separate components, are normal filling, grading, and compacting techniques. Compaction passes that may be required by the various types of compacting equipment vary from 3 to 8.

TABLE 4. WASTE STABILIZATION COSTS (1982)

Function	Approximate cost
Solidification/stabilization	
Chemical fixation	$0.10 to $0.20/gal of sludge Cd, Cn upper portion of cost range Hg, Pb, Zn, Cr lower end of cost range $30 to $70/ton for wastes requiring little pretreatment $50 to $150/ton for wastes requiring pretreatment $100 to $400/ton for very toxic wastes
Bentonite mixing	$0.01 to $0.15/gal, based on $100 to $200/ton bentonite cost
Cement-based	$0.05/lb ($80/ton), cement material cost only. Estimate 1:1 mix waste: cement by weight
Lime-based	$0.05 to $0.20/gal of sludge

Table 5 summarizes costs involved in constructing the bottom and middle layers of impoundment cover. The upper portion of the bottom layer of impoundment cover may consist of a synthetic membrane protected on both sides by at least 6 inches of soil. The cost ranges shown for synthetic liners include the preparation of soil layers, anchoring, field seaming, and quality control testing.

Sand, gravel, and sand-gravel mixtures are most suitable for the middle drainage layer. Fewer total compaction passes are required for this layer than for the lower layer of the impoundment. The top layer of the impoundment cover should be at least 24 inches thick, provide for surface drainage without gully formation, and be planted. Loam soil is assumed to be the soil of choice for the upper layer.

If wastes or waste residues remain when an impoundment is closed, regulations require steps such as planting, combinations of drainage ditches, open channels, berms, and dikes to prevent infiltration through or erosion of the final cover.

TABLE 5. COST DATA FOR CONSTRUCTING BOTTOM AND MIDDLE LAYERS OF A SURFACE IMPOUNDMENT COVER (1982)

Function	Daily output, yd^3	Approximate cost
Dozer backfill with compaction, sheepsfoot roller, up to 300-ft haul, 6- to 12-in. lifts (assumes onsite material source)	510	$1.90/$yd^3$
Buy, load material offsite at pit, haul two miles, place, spread, no compaction		
Structural fill	600	$8.35/$yd^3$
Gravel	600	$6.00/$yd^3$
Bank sand	600	$6.30/$yd^3$
Add for 5-mile haul		$1.40/$yd^3$
Compaction, sheepsfoot roller (4-6 passes per 6 in. layer)	360	$1.55/$yd^3$
Grading		
Dozer - 75 hp	160	$2.90/$yd^3$
Dozer - 300 hp	560	$2.10/$yd^3$
Towed scraper (7 yd^3) 300-ft haul	440	$3.55/$yd^3$
Membrane liners, installed, \$/yd^2		
PVC		$1.65 to $2.55
Chlorinated PE		$3.05 to $4.05
Elasticized polyolefin		$3.15 to $4.20
Neoprene		$6.35
Ethylene propylene rubber		$3.45 to $4.45
Butyl rubber		$3.45 to $4.25

Table 6 shows cost ranges for ditch construction and other surface water controls. The number of ditches will obviously depend on the configuration of the final cover.

TABLE 6. COST DATA FOR ESTABLISHING SURFACE WATER CONTROLS (1982)

Function	Daily output	Approximate cost $/yd^3
Ditch excavation		
4 ft wide, 1/2 to 1 slope 3-4 ft deep: 1/2-yd^3 backhoe	200 yd^3	2.90
Ditch stabilization		
Riprap (machine-placed)	62 yd^3	19.45
Sod	720 yd^2	2.60 (per yd^2)
Gunite with 2-inch mesh, 1 inch thick	650 ft^2	6.90 (per ft^2)
Dike construction		
Dozer backfill, 300-ft haul, air-tamped	240 yd^3	4.80
Buy and load at pit, haul 2 miles, spread with dozer, structural fill	600 yd^3	8.35
Topsoil	600 yd^3	9.00
Compaction, sheepsfoot roller	430 yd^3	1.30
Fine-grading	1600 yd^2	0.50 (per yd^2)
Hauling, spreading of gravel (upslope protection):		
Purchase offsite, haul 2 miles, spread	600 yd^3	6.00

NOTE: Cost includes labor, equipment, materials, and contractor fees.

Post-Closure Care

The primary post-closure care activities expected for hazardous waste landfills and for other types of facilities which have been closed with wastes or waste residues remaining (land treatment facilities and surface impoundments) include the following:

- Annual facility inspection
- Reestablishing cover and vegetation

- Fertilizing
- Mowing
- Groundwater monitoring
- Fence maintenance and repair
- Collecting, removing, and treating leachate

Not all of these activities will be necessary at each facility. For example, at facilities with double liners and properly installed leachate monitoring and collection systems, groundwater monitoring may not be required. Also, if vegetation is properly established during closure and maintained during post-closure, the costs indicated for reestablishing cover and vegetation may never be incurred. The variance in post-closure cost requirements is highly site-specific and depends on the size, engineering characteristics, waste composition and closure procedures at each site. The costs in Table 7 are unit cost estimates that can be applied to post-closure activities. Some of the data in Table 7 were taken from EPA guidance for Subpart H of the interim status standards and updated to 1982 values. It should be noted that the data in Table 8 are for routine facility maintenance procedures and do not include provisions for recovery from unpredictable catastrophes that may occur over the 30-year post-closure period.

TABLE 7. COST DATA FOR POST-CLOSURE CARE OF LANDFILLS AND DISPOSAL FACILITIES WITH WASTES REMAINING ONSITE (1982)

Function	Approximate cost ($)
Inspection/facility visits	45-65/h depends on professional level of personnel
Reestablishing cover and vegetation	350-1740/acre depending on erosion, type of cover and soil
Fertilizing	60-230/acre depending on amount and method of application
Mowing	10-35/acre
Groundwater monitoring	230-700/well
Maintaining and replacing fences	0.33-0.93/ft/yr depending on fence type and climate
Berm maintenance	0.18-0.36/yd^2/yr
Ditch maintenance	2.26-5.28/yd^3/yr
Runoff collection (overland flow)	37-49/acre/yr (1000 acre sites) 294/acre/yr (10 acre sites)

Case Study 1 - Electric Arc Plant Landfill--

The first case involves a landfill, presently used by an electric arc furnace producer of steel, which has been in operation for 30 years. It is located on the plant site, occupies approximately 8 acres, and is adjacent to a river. The landfill is used solely for disposal of wastes generated by the plant.

Landfilled wastes fall under four general categories:

- Electric arc furnace slag
- Electric arc furnace baghouse dust
- Mill scale
- Wastewater treatment pond dredgings

Only the baghouse dust is regulated as a hazardous waste due to its characteristic of extraction procedure (EP) toxicity (lead and cadmium). Generation rates (or landfill deposition rates) are as follows:

Waste	Cubic yards landfilled per year
Slag	14,400
Baghouse dust	6,000
Mill scale	2,400
Dredgings	1,500

The quantity shown for dredgings is prorated over a five-year period since the wastewater treatment pond is dredged only once every five years. It is important to note here that nonhazardous wastes were included in this plan for purposes of determining landfill life expectancy. The costs for management of final inventories of nonhazardous wastes are not included in the closure cost estimate.

It was apparent from the outset of the closure planning effort that the use of on-site materials for cover would be a great economic advantage. To accurately estimate the quantities and characteristics of on-site materials, primarily clay, as well as adequately implement a groundwater monitoring program, a detailed subsurface profile of the landfill and surrounding area was prepared. The profile was composited from existing boring information from the plant's geotechnical contractor and was confirmed through data collected during construction of the groundwater monitoring system around the landfill.

In adjacent areas of the plant site, an adequate amount of clay is available for use as final cover. The clay is typically very moist and relatively compressible. Liquid limits vary from 27 to 44 percent and plastic limits from 16 to 24 percent. The coefficient of permeability of this clay averages 1 x 10^{-8} cm/s, which is adequately "impermeable" for use as a final cover.

Before placing the lower clay layer, the upper surface of the landfill will be graded to a slope of 2 to 3 percent to promote runoff and reduce (or eliminate) infiltration into the landfill. This final grade slope is also designed to minimize erosion from high surface flow velocities. It is estimated that 26,000 yd^3 of clay will be required to apply a 2-foot cover over the landfill. After the clay is applied, it will be graded and rolled for compaction and a drainage layer will be installed. A 2-foot neutral or mildly alkaline silt loam will then be applied to the cover to support the growth of grass. Approximately 26,000 yd^3 of this top soil will also be required and will be obtained locally on-site. Compacted slag will be used on perimeter slopes with greater than 10 percent slopes to minimize erosion. Slag can be obtained on-site for no cost and will provide stable embankment slopes. Figure 1 shows the plan and cross sectional views of the landfill including the final cover.

In addition to placing the final cover to the landfill, which is the most costly of all closure activities, the following activities are also planned specifically during and in conjunction with closure of the landfill:

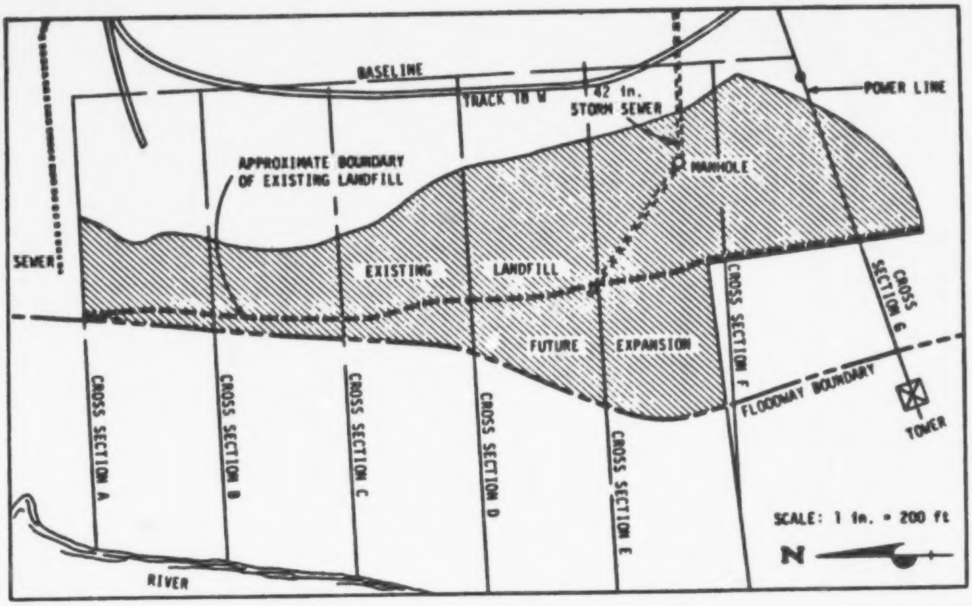
- Groundwater monitoring
- Removal/disposal of all potential hazardous wastes not yet landfilled
- Decontamination of equipment and affected areas
- Spreading of grass seed, fertilizer, and straw
- Security
- Closure certification
- Administration
- Contingencies

It was assumed in deriving closure costs that the plant would provide labor and equipment for all closing operations. The above closure-related activities are expected to cost approximately $15,000 per acre or $120,000 (1982 dollars).

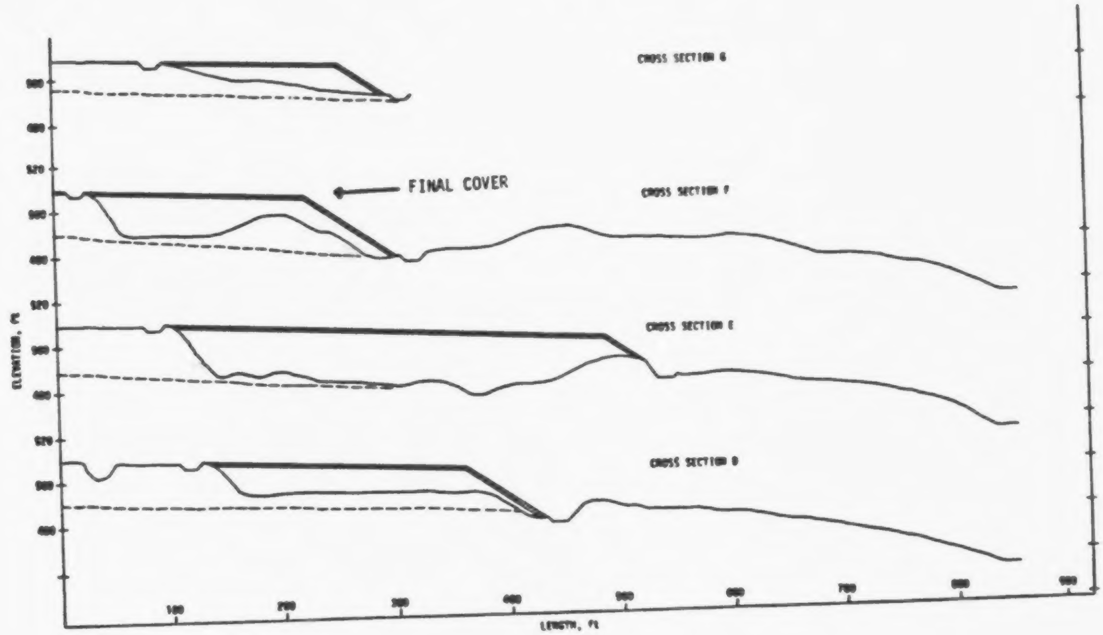
Additionally, post-closure care of the landfill is planned for a period of 30 years following closure. The following activities will be accomplished during the post-closure period:

- Periodic inspections
- Grass mowing
- Cover repair (soil replacement, compaction, fertilizer, grass seed)
- Embankment and diversion ditch repair
- Groundwater wells
- Groundwater monitoring
- Security
- Contingencies
- Administration

It was assumed in deriving post-closure costs that all necessary labor, materials, and equipment will be provided contractually. The annual cost of post-closure care is estimated to be about $7,500 (1982 dollars), or about $1,000 per acre.


BASELINE
TRACK 18 W
42 in. STORM SEWER
POWER LINE
APPROXIMATE BOUNDARY OF EXISTING LANDFILL
MANHOLE
SEWER
EXISTING LANDFILL
FUTURE EXPANSION
CROSS SECTION A
CROSS SECTION B
CROSS SECTION C
CROSS SECTION D
CROSS SECTION E
CROSS SECTION F
CROSS SECTION G
FLOODWAY BOUNDARY
TOWER
SCALE: 1 in. = 200 ft
N
RIVER

Plan view



Cross-sectional view (D-G only)

Figure 1. Plan and cross-sectional views of landfill.

Case Study 2 - Open Hearth Sludge Lagoon--

The second case involves an open hearth scrubber sludge storage lagoon. The activities conducted in connection with closure included:

- Quantitatively and qualitatively characterizing scrubber sludge stored in a surface impoundment (lagoon)
- Determining the most reasonable final disposal alternatives for the sludge
- Evaluating the depth of contamination in the clay liner

This steel-making facility has been closed, and following shutdown the Federal regulations governing the management of hazardous waste were promulgated. The objective of the first study was to accurately estimate quantities of sludge and standing water in the lagoon, but more importantly, to analyze the sludge for EP toxicity to determine if it was hazardous waste. The sludge lagoon layout is shown in Figure 2.

The total plan area of the lagoon is approximately 0.75 acre. Standing water in the lagoon was estimated to total 75,000 ft^3 (560,000 gallons). Sludge was estimated at 5,000 yd^3.

Twelve samples of sludge were collected; six above the waterline and six below. Half of the samples were taken three feet below the surface using an eggshell core sampling device. These samples were composited into two samples that were analyzed for EP toxicity (metals only). Additionally, an analysis was performed using deionized water in place of acetic acid in the EP test. Each sample was then split for duplicate analysis. The standing water composite was composed of 12 individual samples taken from two depths at each of six locations. The water composite was split for duplicate analysis and analyzed for the same metals as in the EP test. The results of these analyses are shown in Table 8.

The results indicated that in the sludge, only lead approached the maximum allowable limit set by the RCRA regulations. Lead was, however, measured below the limit of 5 mg/l in the EP extract.

The state EPA sampled the sludge over the next few months and found it just over the limit for lead. Split samples with the agency resulted in the same discrepancy. The steel company made the decision to proceed as if the waste was hazardous to avoid all possible future liabilities.

The lagoon was emptied of standing water by pumping and discharge to a river (previous analysis showed water quality was acceptable). The sludge was allowed to dry and was excavated and transported to a RCRA-permitted landfill. The clay liner was intended to be left in place; however, the agency required a sampling and analysis program to determine depth of possible contamination.

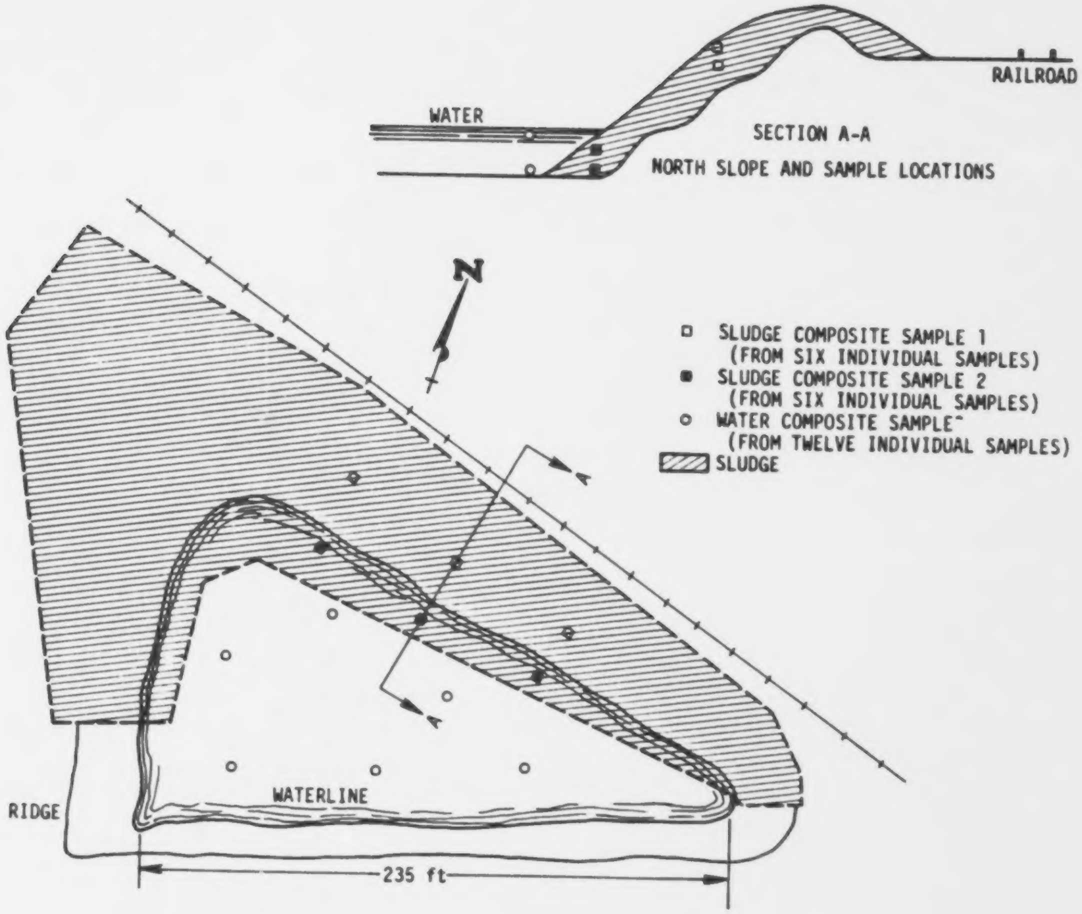

WATER
RAILROAD
SECTION A-A
NORTH SLOPE AND SAMPLE LOCATIONS
N
□ SLUDGE COMPOSITE SAMPLE 1 (FROM SIX INDIVIDUAL SAMPLES)
■ SLUDGE COMPOSITE SAMPLE 2 (FROM SIX INDIVIDUAL SAMPLES)
○ WATER COMPOSITE SAMPLE (FROM TWELVE INDIVIDUAL SAMPLES)
▨ SLUDGE
A
A
WATERLINE
RIDGE
235 ft

Figure 2. Sludge storage area layout and cross section of north slope (Note: cross section not to scale).

TABLE 8. METAL CONTAMINANT CONCENTRATIONS IN EP TEST EXTRACTS
(values reported in mg/l)

Extract	Sludge - underwater		Sludge - above water		Pond water	Allowable conc.
	Acid	Water	Acid	Water	a	
Metal						
As	0.004-0.007	0.016-0.198	0.003-0.003	0.025-0.091	0.011-0.016	5.0
Ba	0.117-0.145	0.297-0.452	0.104-0.129	0.332-0.362	0.030-0.042	100.0
Cd	0.175-0.258	<0.0008	0.083-0.209	<0.008	0.001-0.002	1.0
Cr	<0.001	<0.001	<0.001	<0.001	<0.003	N/A
Cr^{+6}	<0.001	<0.001	<0.001	<0.001	<0.003	5.0
Pb	3.11 -3.99	<0.001-<0.008	0.21 -2.40	<0.001-<0.006	0.022	5.0
Hg	<0.001	<0.001-0.006	<0.001	<0.001	<0.001	0.2
Se	0.007-0.012	0.005-0.009	0.009	0.005-0.008	0.007	1.0
Ag	<0.002-0.012	<0.002	<0.002-0.007	<0.002	<0.002-0.002	5.0

[a] Total metal concentration (not extract) was determined for pond water samples.

The liner was sampled at 12 locations, in 3-inch increments, for a total depth of 2 feet. Additionally, two background samples were taken for comparison. The analyses included total lead and EP toxicity (lead only) for each sample; however, the uppermost samples were analyzed first and the data reviewed before proceeding. The results of the first round of analyses are shown in Table 9. It is interesting to note the fairly consistent correlation between total and EP toxicity concentrations, as well as the comparison of background concentrations with those of the clay liner.

TABLE 9. ANALYSIS OF CORE SECTIONS FROM LAGOON LINER

Sample	Total recoverable lead, μg/g	EP toxicity extractable lead, mg/l
Background	146	<0.3
Background	192	<0.3
1	62	<0.3
2	54	<0.3
3	230	<0.3
4	68	<0.3
5	2730	8.6
6	94	<0.3
7	52	<0.3
8	1520	1.3
9	50	<0.3
10	40	<0.3
11	55	<0.3
12	46	<0.3

Total recoverable lead by EPA Methods 3050 and 7420.
EP toxicity extractable lead by EPA Methods 1310, 3010, and 7420.

Only one location showed EP toxicity concentrations of lead above the maximum allowable (5 mg/liter), indicating that the clay in this area was a hazardous waste and must be removed for offsite disposal. The 3- to 6-inch layer at this sample location was analyzed and lead was found to be nondetectable. In order to be conservative, the owner decided to excavate the liner in the area directly adjacent to sample 5 to a depth of 3 inches for offsite disposal.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

(1) Data for reviewing closure and post-closure costs of hazardous waste management facilities. PEDCo Environmental, Inc. and A.T. Kearney, Inc. August 1983. EPA Contract 68-01-6515, Work Assignment R07-003.

(2) Final draft guidance for subpart H of the interim status standards for owners and operators of hazardous waste treatment, storage, and disposal facilities. General Research Corporation. November 1981.

(3) Handbook of remedial action at waste disposal sites. U.S. Environmental Protection Agency, EPA-625/6-82-006, June 1982.

ABSTRACT

CLAY LINER PERMEABILITY ASSESSMENT: A STUDY OF ACCELERATED TESTING FOR CHEMICAL COMPATIBILITY WITH AN INDUSTRIAL WASTE

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Fluids produced from wastes were used in accelerated (high pressure), anaerobic permeability tests with three disposal site soils obtained from soil cores. Comparison tests measuring hydraulic conductivity were performed to determine behavorial differences of the candidate soil liners with waste leachate and water. Test results were used to evaluate waste compatibility with soil with emphasis placed on identifying fatal flaws in expected field liner performance. Transparent permeameters allowed visual observation of liner changes during six-month laboratory permeability tests for evidence of failure mechanisms. Periodic checks of the clay for piping, back diffusion, shrinking/swelling, cracking and dissolution were made with permeability measurements. To corroborate observations of external changes before and after permeability tests, clay Atterberg limits were performed to determine structural swelling or collapse. Also, in long-term batch leaching tests, silicon and aluminum concentrations in the waste leachate in contact with soils were measured monthly to monitor loss of atoms from the internal clay structure. At the end of this test x-ray diffraction was performed on the soil to determine differences in crystalline components due to interaction during the accelerated batch leaching tests. The waste leachate was monitored after percolation through the soils in column studies for indications of attenuation of contaminants in soils that did not provide an adequate impervious barrier.

One soil physically contained the two waste leachate types by providing an impermeable barrier. The other two soils, while not providing strong physical barriers, did contain the leachates through chemical attenuation of the trace contaminants in the leachate in column leaching tests. Both mechanisms of containment should be effective in providing protection of groundwater resources.

INTRODUCTION

The use of compacted native soils has been demonstrated to be a feasible method of retarding leachate and waste liquid components from excessive leakage and subsequent pollution of groundwater. Described here is an approach for evaluating in the laboratory a natural soil liner's performance expected in the field. A specific case study is described using paper mill waste. However, the same experimental approach would apply to other waste types. The major purpose of the liner evaluation study was to provide information on performance of specific liners with specific wastes and guidance in the selection of liners based upon the current state-of-the-art of liner technology.

While nonhazardous steel wastes may differ from paper mill wastes by containing higher concentrations of trace metals and structurally different organic species, this experimental approach provides a set of tests which allow rapid identification of failure mechanisms which are common to all wastes.

BACKGROUND

The purpose of lining a waste disposal impoundment is to prevent waste contaminants from leaving the site and entering natural ground water systems near the site. In their performance, liners function by two mechanisms: (1) impedance of flow of the pollutant carrier (usually water) into the subsoil, and/or (2) attenuation of suspended or dissolved pollutants so that the exiting leachate contains contaminants within acceptable ranges for groundwater (1).

The first liner function is attained by constructing a material with low permeability. The sorptive or attenuative capability relies on the chemical composition and mass of the liner. Soil liners generally function by both mechanisms. Soils generally have a large capacity to absorb materials of different types, but some soils do not provide an impermeable boundary. However, a greater thickness of a soil layer beneath the disposal impoundment can result in the low flux of a contaminant through the liner. A good soil liner will contain a minimum of 25-28% clay-size particles by weight (1). The clay-size fraction has a relatively large surface area and the mechanical behavior of a clayey soil is dependent on the physio-chemical characteristics of the surface.

Soils used as liners also must have acceptable engineering properties. The soil consistency differs with moisture content, and the degree of hydration of clayey soils has a direct effect upon the liner's compressive strength. The plastic limit (soil moisture content just below which the soil is friable and just above which the soil is plastic) and the liquid limit (soil moisture content just below which the soil is barely plastic and just above which the soil flows) are also valuable in assessing the engineering characteristics of soils (2). The soil properties can be altered by mechanical compaction, which affects the permeability. Each soil has a unique laboratory moisture/density relation, i.e., Proctor compaction curve, which defines optimum moisture amd maximum dry density for design considerations. Soils permeability is a numerical measure of the ability of the soil to transmit a fluid. The permeability is dependent on both the soil properties and leachate properties. A good liner will usually possess a permeability coefficient of 1×10^{-7} cm/sec or less when it is tested with a simulated (or actual) waste fluid.

APPROACH

Each waste and soil liner was characterized for pertinent properties. However, the main thrust of the approach to liner evaluation was determining the interactions of liners and wastes. (These tests are also applicable to specific steel waste interaction with soils.) The major focus of the liner evaluation involved short-term and long-term compatability studies. The liner evaluation criteria for waste characterization, soil properties, and compatibility studies are given below.

Waste Leachate Properties

The leachate and the contaminants it contains can be aggressive to liner materials. Water, itself, can be an aggressive constituent, causing a liner material to swell. The initial whole sample compositions of actual waste composites were used in the liner study to identify possible reactive chemical constituents that might preclude the use of clay soils as liners thus requiring synthetic liners. Waste leachates generated using the ASTM procedure were used in the short- and long-term liner compatibility studies. The compositions of column leachates were used to screen for long-term leachate composition changes accompanying anaerobic saturated conditions and provide soil attenuation data as necessary.

Soil Properties

Each candidate liner was characterized for the soil properties listed in Table 1. Included in the table are synopses of the test objectives.

Short-Term Waste Leachate/Soil Compatibility

The initial compatibility tests consisted of a set of laboratory experiments designed to determine the initial behavioral differences in the soil when it is interacted with a waste leachate. Short-term compatibility of liners with waste leachate was evaluated by comparing the liners' properties after wetting with water to their properties after wetting with waste leachate. Following wetting with each liquor, the liners were tested for permeability, internal structural changes, and plasticity.

Permeability-- A test method for examining effects of waste leachates on liner permeabilities, developed by Matrecon, Inc. for the U.S. EPA, was used in liner evaluation (1). Liner materials were compacted in transparent peremeameter (three inch diameter) at optimum compacted density (ASTM Method D-

TABLE 1. SOIL PROPERTIES DETERMINED FOR CANDIDATE NATURAL LINERS

Soil Property	Test Method	Purpose
Particle size distribution	Sieve and hydrometer (4)	Estimates percent sand, silt and clay
Compaction test	Compact liner at different moisture contents and measure compacted density (5)	Determines the moisture content which results in maximum compacted density at a given compactive effort
Atterberg Limits	Measure of plastic and liquid limit (6,7)	Defines effects of varying water content on soil consistency
Chemical Properties		
Percent organic matter	Titration (8)	Organic matter in liners may attenuate organics from leachates
Soil pH	Electrometric (9)	Alkalinity of a soil will affect its ability to attenuate chemical contaminants
Cation exchange capacity	Sodium saturation followed by ammonium extraction; analyze for sodium (8)	Estimates the extent to which the liner may exchange (remove) cations from the leachate
Major Exchangeable Bases	Ammonium extraction; analyze for sodium, potassium, magnesium, and calcium (8)	Estimates the liners capacity to exchange ions on base sites and identifies major ions absorbed on clay before interaction
X-ray powder diffraction	X-ray diffractometer	Identifies clay minerals in liners

698). The appropriate liquor (water or waste leachate) was placed in the permeameter over the compacted soil and forced through the soil at slightly elevated head pressure by using nitrogen at a pressure of 3 to 5 psig.

Internal Structural Changes--Internal structural changes were investigated using X-ray diffraction. First, to identify the clay minerals present in each candidate liner, a powder pattern of a representative sample of the bulk soils was obtained. These patterns also were used to identify regions showing dioctahedral structures susceptible to possible interaction with organic species in the waste leachate. The second set of X-ray diffraction experiments was performed to determine the initial effect of waste leachate on the candidate liners. If a substantial interlayer spacing decreased for the second set of data, shrinkage cracks may be anticipated for that particular liner-waste combination. (This method was performed again at the end of long-term accelerated batch leaching to determine changes in soil crystallinity due to extended shaking with a 10:1 ratio of leachate with soil.)

External Property Changes--The plasticity (Atterberg Limits) was evaluated for each candidate liner with the appropriate waste leachate, as well as with water; large differences in the plasticity with water and waste fluid would indicate possible expected failure in the field behavior of the liner due to changes like shrinking or swelling.

Long-Term Compatibility

Long-term waste leachate/liner compatibility was assessed by continuing to monitor soil permeability and failure mechanism observed in soils undergoing permeability tests, and by performing accelerated batch leaching tests of the soils with leachate, monitoring chemical breakdowns of the soil and internal structural changes in the clay minerals in the soils.

Permeability and Failure Mechanism Observation--Permeability measurements were taken once per week to note changes due to waste-liquor interactions. At the end of six months testing, the soil cores were visually examined for indications of the failure mechanisms.

Accelerated Batch Leaching--The accelerated long-term compatibility involved leaching of the liners with water or waste leachate in a batch extraction apparatus. The liners were agitated for two months at approximately a 10:1 liquid-to-solid ratio. Aliquots were removed monthly for analysis of aluminum and silicon concentration to assess chemical degradation of the clays in the soils. At the end of the two months of leaching, the soils were separated from the liquor and examined for physical or structural changes using X-ray powder diffraction.

Leachate/Soil Interaction--Prior to contacting the groundwater, the contaminants in the wastes must migrate through soil liners where some degree of attenuation (reduction in concentration) will take place. Even after the contaminants enter the groundwater, soil attenuation mechanisms will continue to reduce the contaminant levels. For nonhazardous wastes a desirable disposal practice is to utilize the natural attenuation processes of the soil media beneath the disposal site. These attenuation processes include precipitation by changes in the aqueous environment, adsorption onto soil surfaces, filtration of contaminants by tightly packed soils, and dispersion and diffusion within the unsaturated zone and in the groundwater.

The approach taken in this project for estimating the degree of soil attenuation was to simulate the leaching and soil attenuation processes through column studies using actual samples of solid waste and soil. The concentration of contaminants found in the column leachates and subsequent soil attenuate served as indicators of the soils' ability to reduce contaminant levels entering the groundwater.

Leachate aliquots were collected at the end of each day, filtered, and refrigerated. For every liter of leachate collected, the following index parameters were analyzed: pH, conductivity, redox potential, and TOC. The first aliquots from each column were characterized for inorganic species. Subsequent aliquots were analyzed only for those inorganic and organic species found in measurable concentrations in the first aliquot.

DISCUSSION OF LINER TEST RESULTS

The discussion of results is separated into sections on waste character, soil properties, initial compatibility and long term compatibility. These tests were designed to evaluate two site soils geographically close to waste generation points. Therefore, this case study involved evaluation of Waste #1 with Soil #1, Waste #2 with Soil #2, and from another site Waste #3 and Waste #4 with Soil #3.

Waste and Leachate Character

Waste #1 consisted largely of organic material with minor quantities of calcium and silicon compounds. Waste #2 contained mainly calcium, magnesium and silicon compounds, with higher trace elements concentration. Waste #3 contained mainly calcium compounds. Waste 4 consisted of mainly calcium, sodium, silicon, aluminum and trace metals.

Waste Leachates--Leachates were obtained from the wastes by ASTM Method A (10) and these chemical compositons are given in Table 2. (This method uses a 20:1 liquid-solid ratio with no pH adjustment and deionized water as the liquid. Chemical analysis of leachate from Waste #1 disclosed calcium, sodium, potassium, and hydrogen sulfide as the major dissolved species. The total dissolved solids (680 mg/L) and total organic carbon (42 mg/L) had elevated concentrations with a pH of 11.2. Leachate from Waste #2 had a TDS content of 480 mg/L, and the pH was again 11.2. Calcium, sodium, potassium, and hydrogen sulfide were the major dissolved species. Waste #3 and #4 had a TDS content of 1,100 and 1,500 mg/L respectively. They both contained major concentrations of sodium and potassium with pH's of 10.1 and 11.3 respectively.

TABLE 2. CHEMICAL ANALYSIS OF ASTM EXTRACT OF LINER STUDY WASTES (mg/L)

Species	Concentrations			
	Waste #1	Waste #2	Waste #3	Waste #4
• Major/Minor Elements				
Calcium	150	62	3.0	9.5
Iron	<0.008	<0.008	1.2	0.19
Potassium	5.6	24	13	29
Magnesium	<0.03	0.059	0.72	<0.034
Sodium	130	94	350	440
• Trace Elements				
Silver	<0.002	0.005	<0.002	<0.002
Aluminum	<0.05	0.11	2.3	8.7
Arsenic	<0.003	<0.003	<0.003	<0.003
Boron	<0.01	0.21	<0.01	<0.01
Barium	0.17	0.42	0.035	0.034
Cadmium	<0.002	<0.002	<0.002	<0.002
Chromium	<0.001	0.005	0.048	0.001
Copper	<0.001	0.012	0.045	0.017
Mercury	0.0008	0.0006	<0.0002	<0.0002
Manganese	<0.001	<0.001	0.46	0.14
Molybdenum	<0.002	<0.002	<0.002	<0.002
Nickel	<0.003	<0.003	0.007	0.023
Lead	<0.002	<0.002	<0.08	<0.002
Antimony	<0.03	<0.03	<0.03	<0.03
Selenium	<0.003	<0.08	<0.003	<0.003
Zinc	<0.003	<0.003	<0.003	0.01
• Water Quality Parameters				
Hydrogen Sulfide, H_2S	6	13	14	18
Total Dissolved Solids (TDS)	680	480	1100	1500
pH	11.2	11.2	10.1	11.3
Total Organic Carbon (TOC)	42	7	134	98
Total Organic Halogen (TOX)	0.13	0.10	1.3	<0.05
Fluoride, F	<0.1	0.1	0.2	0.3
Nitrate, NO_3	0.01	0.01	<0.01	0.08
Color	180	5	1500	1500
Tannin	10	3	31	46

Soil Properties

A summary of the properties of the soil liners is given in Table 3. These properties were identified to aid in interpretation of soil-waste leachate interactions. Tests were performed on soil borings at expected excavated soil liner levels.

Particle Size Distribution--Results from particle size testing showed that Soil #3 (from a different site) contains much more clay than Soils #1 and #2 (from the same site). Although a higher clay content is desired, the presence of silt with clay in the natural soil should reduce the shrink/swell problems experienced with clays while still providing fairly large surface area for attenuation reactions.

Compaction--Moisture-density relation for all of the soil liner candidates correspond to a somewhat impervious barrier. These data correlate with the known concepts that the more granular the soil (as with Soil #1 and Soil #2), the higher the maximum density and the lower the optimum moisture, and the finer the soil (as with Soil #3), the less defined the maximum density and the lower the slope of the curve of the density as a function of the moisture content (1,2). For Soil #3, increasing the moisture requirements during compaction causes the density to again become more critical, e.g., a small decrease in density (1 percent) may result in an increase in permeability by one order of magnitude.

Atterberg Limits--Preferred Atterberg limits for liner performance require a liquid limit between 35 and 60 percent water, and a plasticity index above the A-line as shown in Figure 1 (1). While Soil #3 falls in the preferred zone, Soil #1 and Soil #2 have liquid limits too low to fall into the preferred zone.

Organic Matter Content--Soil properties including absorption and retention of water, reserves of exchangeable bases, and stability of soil structure are dependent to some degree on the quantity of organic matter present. The organic matter contents for the three soil borings down to 50 feet were expectedly low (¼1 percent), with Soil #3 showing slight superiority.

Soil pH--The soil pH of the Soil #1 and #2 were practically neutral, while Soil #3 was slightly below neutral (6.20). The pH of a soil generally decreases with increasing concentration of neutral salts, e.g., NaCl, $CaSO_4$.

Cation Exchange Capacity--Cations held on the surface of soil minerals and within the crystal framework can undergo exchange reactions reversibly in salt solutions and acids. The cation exchange capacity (CEC) is defined as the sum of the exchangeable cations of a soil. A high CEC generally denotes a high clay content and potentially a high capacity to attenuate contaminants. Soils vary in CEC from ¼1.0 to ½100 milli-equivalents per 100 g. The CEC of the Soil #3 is a medium level soil, and Soil #1 and #2 are low.

TABLE 3. RESULTS OF SOIL PROPERTY TESTS ON CANDIDATE LINERS

Soil Property	Soil #1	Soil #2	Soil #3
Particle Size Distribution			
% Sand	15	13	12
% Silt	68	70	48
% Clay	17	17	40
Compaction Moisture/Density Relation			
Optimum Moisture (%)	14	13	18
Maximum Dry Density (pcf)	115	116	110
Atterberg Limits			
Liquid Limit (%)	30	30	38
Plastic Limit (%)	21	21	17
Plasticity Index (%)	9	9	2
Organic Matter Content (%)	0.3	0.4	0.6
Soil pH	7.3	7.1	6.2
Cation Exchange Capacity (meq/100g)	11	12	24.6
Major Exchangeable Bases (meq/100g)	15	12	20
Clay Minerals Present	Ca-substituted nontronite (iron-rich montmorillonoid) kaolinite microcline (alkaline feldspar) muscovite (dioctahedral mica) quartz dolomite	Ca-substituted nontronite (iron-rich montmorillonoid) kaolinite microcline (alkaline feldspar) muscovite dioctahedral mica) quartz dolomite	Ca-substituted nontronite (iron-rich montmorillonoid) kaolinite microcline (alkaline feldspar) muscovite dioctahedral mica) quartz dolomite

Major Exchangeable Bases--Exchangeable bases are defined as the alkali and alkaline earth metals, principally calcium, magnesium, potassium, and sodium, that are attached to the clay and organic constituents of the soils and which can be exchanged with each other and with other positively charged ions in the soil solution. The major exchangeable bases (MEB) in the soils accounted for almost the entire cation exchange capacity.

Clay Mineral Identification--Clay minerals were identified in the soils using X-ray diffraction in order that any microstructural changes due to subsequent leachate interaction could be monitored. Originally, all of the soils contained kaolinite, microcline (alkali feldspar), muscovite (dioctahedral mica), and significant amounts of quartz. The clay fraction present behaved as a dioctahedral expanding smectite, probably nontronite (the dioctahedral structure is indicated by the 060 peak at approximately 62°, or 1.50 A). Electron diffraction X-ray spectroscopic scan of elements in the samples (Mg, Al, Si, K, Ca, Ti, and Fe) and the sample color implied the presence of nontronite, an iron-rich montmorillonoid. The x-ray diffraction of these samples indicated calcium substitution.

Initial Compatibility Results

The initial compatibility testing involved comparisons of each liner's behavior after wetting with water to its properties after wetting with the appropriate waste leachate. This matrix due to geographic location of process and adjacent proposed landfill areas required testing of: Waste #1 with Soil #1, Waste #2 with Soil #2, Waste #3 with Soil #3, and Waste #4 with Soil #3. Each liner was tested for permeability, internal structural changes in its clay minerals, and changes in plasticity.

Internal Structural Changes--Initial reaction of waste leachate with the candidate liners did not produce marked differences from exposure to water for any of the soil liner candidates. X-ray diffraction results showed some minor changes which included shifts indicating possible swelling of Soil #3 and magnesium to calcium exchange on dolomite. These results indicate that no immediate internal structure changes are a result of leachate interaction and the liners are stable in water and initial waste leachate interaction. These soils showed good orientation and high intensity due to stability of suspensions in the x-ray powder pattern.

External Property Effect--To evaluate the effect of waste leachate interaction on the external engineering properties of the candidate liners, the Atterberg limit tests were performed and the results compared to soil performance with water. In no case did the waste leachates produce major difference in the plasticity properties of the liner candidates; results were indicated in Figure 1.

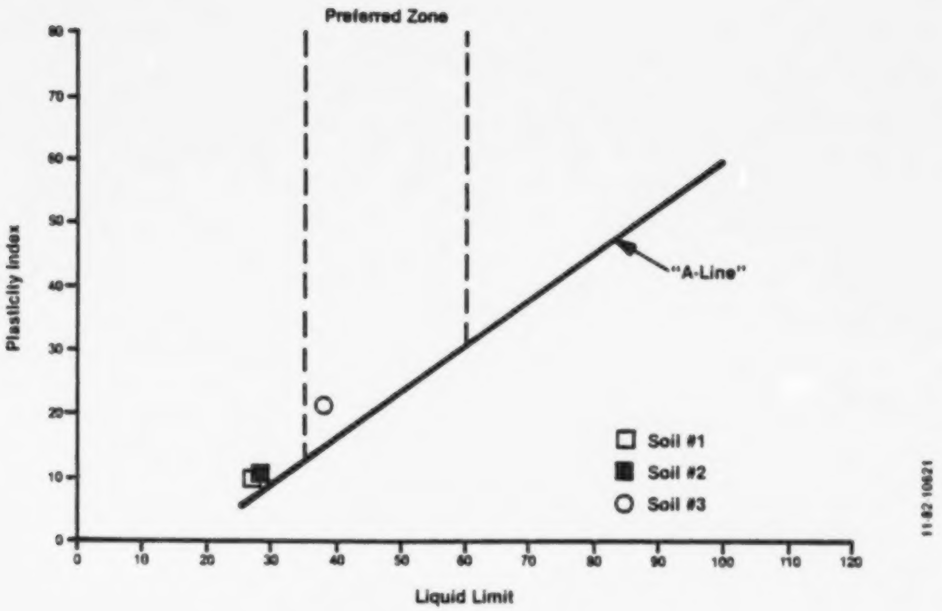

Figure 1. Plasticity Soil Liner Candidates

Long-Term Compatibility

To evaluate the long-term compatibility of the candidate liners with waste leachate, permeability was monitored weekly for six months. At the end of six months, visual observations of the liners in the permeability tests were recorded.

Accelerated batch leaching tests were also performed with the soils and leachates. Under constant agitation in excess leachate (10:1 liquid-solid ratio), the liners were tested for long-term compatibility by (1) measurement of aluminum and silicon in leachate which would imply structural clay breakdown, and (2) microstructural changes in the clay minerals that would show up during X-ray diffraction analyses.

Permeability measurements after one week of testing with water as the leachate for Soil #1 was 1.1 x 10^{-7} cm/sec; Soil #1 permeability is marginally low enough to provide an impervious barrier. When tested with Waste #1, the permeability was 1.5 x 10^{-7} cm/sec after one week of testing, indicating that the initial liner performance was not severely perturbed by Waste #1 leachate. When tested after one week the permeabilities of Soil #2 were 7.4 x 10^{-8} cm/sec with water and 8.5 x 10^{-8} cm/sec with Waste #2 leachate; these are highly acceptable values. After one week of interaction of Soil #3 with water, Waste #1 and Waste #2, the permeability was extremely low (¼10^{-9} cm/sec) for all fluids tested.

Long-Term Permeability Behavior--After six months of testing, the permeability coefficient of Soil #1 with Waste #1 leachate was still 1.2 x 10^{-7} cm/sec. Consistency in the value indicates stability; however, the permeability is only marginally acceptable. (Because there is 50 feet of soil between the waste and ground water, computer water balance modeling indicates that no leachate should leave the disposal site during the site lifetime; therefore marginal permeability is probably acceptable.)

Soil #1 had developed moderate cracks possibly due to dissolution of dolomite from the soil; no shrinkage or swelling was observed. Soil #1 also appeared to be undergoing slight back diffusion of clay into the leachate above the liner. These visual changes indicate that failure mechanisms may occur over long periods of continual waste leachate/soil interaction.

The final permeability for Soil #2 with Waste #2 leachate was 8.5 x 10^{-8} cm/sec, the same as the initial measurement showing good stability in behavior. Soil #2 did not shrink or swell and showed only slight back diffusion. (While back diffusion on a major scale can indicate that the liner's clay affinity is much greater for suspension in leachate in the waste body as opposed to staying in a compacted layer beneath the waste, slight back diffusion should not result in failure of the liner.)

The final permeabilities for Soil #3 with Waste #3 leachate and Waste #4 leachate were 4.4 x 10^{-9} cm/sec and 1.3 x 10^{-9} cm/sec respectively. Soil #3 is highly impermeable and provides a good physical barrier for both waste leachates. With Waste #3 leachate and Waste #4 leachate, Soil #3 showed slight shrinkage over six months.

Accelerated Batch Tests--Aluminum and silicon concentrations measured in the accelerated batch leach testing were analyzed monthly. These concentrations were extremely low and imply no chemical breakdown in any of the liner candidates. These results agree with the X-ray diffraction results which also indicate that no major changes in the clay structures are occurring.

Auxillary Studies (Column Attenuation)-- Because Soil #1 and Soil #2 did not provide superior liner qualities as an impervious barrier, the soil's ability to attenuate contaminants in the waste became an important factor in evaluating the possible effectiveness of the candidate liners.

Column tests simulated the dynamic leaching process at the proposed disposal site and provided an estimate of the ability of the local substrate materials to attenuate contaminants from leachate as it migrates downward toward the water table. Four columns were operated using Waste #1 and Soil #1 from the proposed disposal site for the Waste #1. One column contained waste only, and the other three columns contained layers of waste and soil. These three columns provided for duplicate columns and different leachate flow velocities. Comparison of leachates from the column containing waste only with the leachate from the columns containing both waste and soil showed that the soil provides significant attenuation of TOC, TDS (as indicated by conductivity), sodium, and barium (see Figure 2). Attenuation was greatest during the initial pore volume displacements (initial flushing of the columns). The pH of the waste leachates from the waste-only column decreased substantially for all parameters (except pH). The concentrations of the total sulfur were substantially the same in leachates from both types of columns, indicating little or no attenuation of this parameter.

Two leaching columns were operated for the Waste #2; one column contained waste only, and the other contained a layer of waste and a layer of soil. Comparison of the leachate from the two columns showed the same results as for the columns containing Waste #1. TOC, TDS (as indicated by conductivity), Na, and Ba were attenuated by the soil layer, particularly in the initial pore volume displacement (see Figure 3). The pH, which was 10 or higher in the waste leachate, was at or near 7 in the waste/soil leachate. Total sulfur, on the other hand, was not appreciably reduced when the leachate was exposed to the soil. In general, the concentrations of the parameters in leachate from the waste again decreased with increased leaching.

Conclusions

The major conclusions for the Waste #1 liner candidate is that the Soil #1 demonstrates marginally acceptable liner performance. Soil #1 does not have as much clay as a "good" liner should have; its liquid limit and plasticity index are somewhat lower than preferred, and its permeability falls at the margin of acceptability. However, this liner is acceptable because (1)

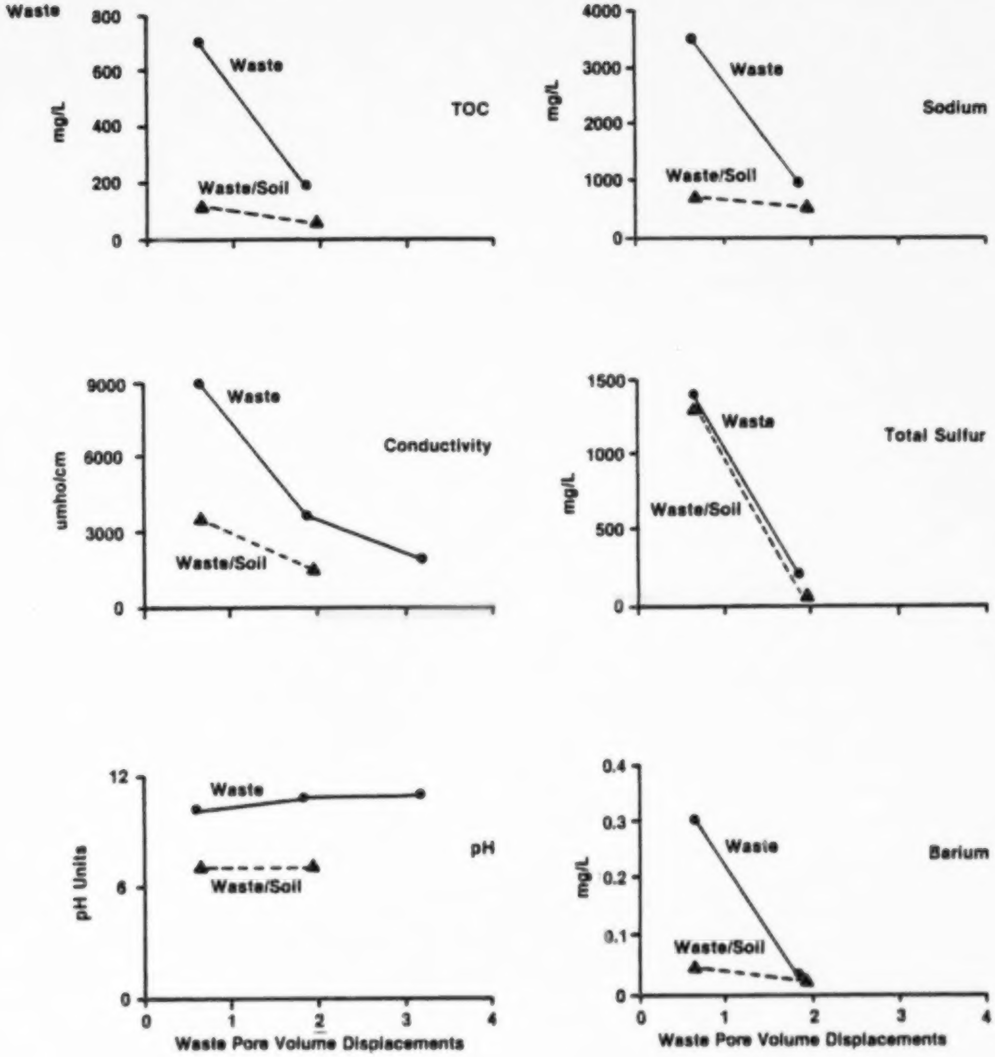

Figure 2. Leachate/Soil Interactions for Soil #1 with Waste #1

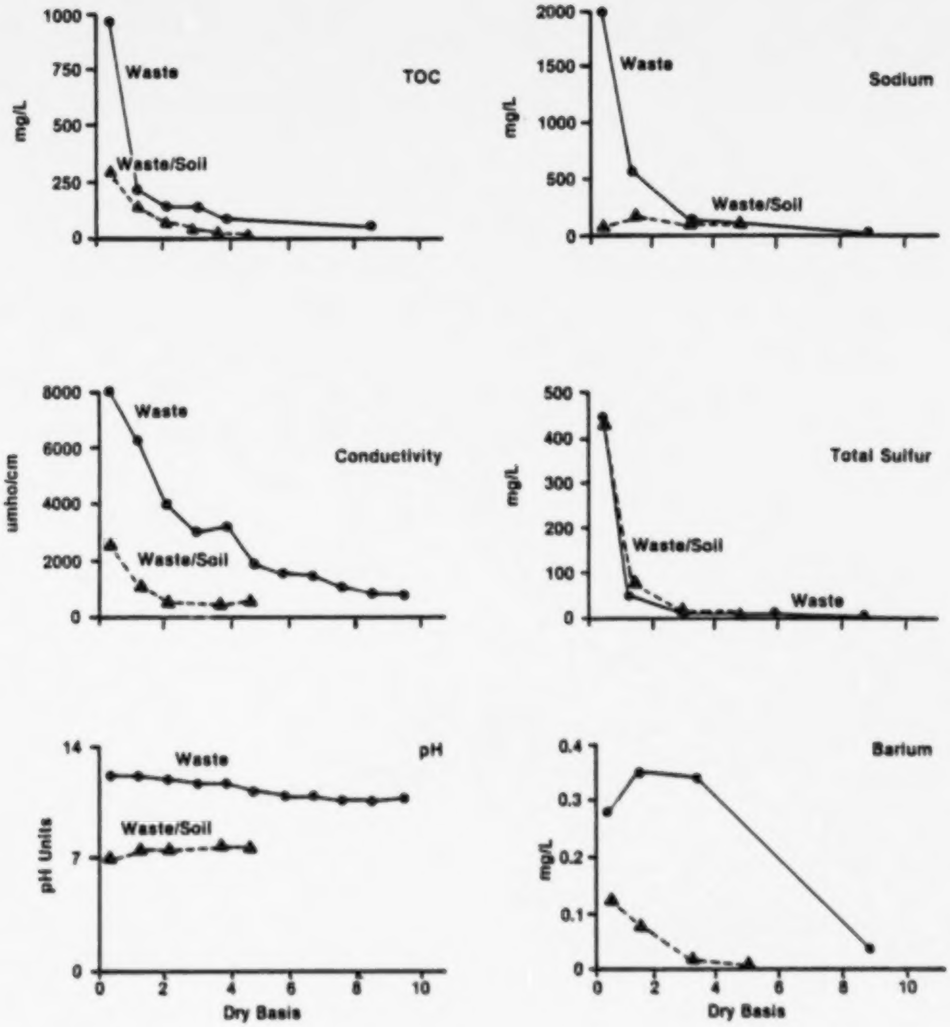

Figure 3. Leachate/Soil Interactions for the Soil #2 with Waste #2

it is capable of attenuating contaminants in the waste leachate; and (2) it is underlain with a large depth of soil above the groundwater at the actual site.

The Waste #2 liner candidate is acceptable. While Soil No. 2 is lower in clay content than preferred, and has a lower liquid limit and plasticity index than preferred, it has very acceptable permeability properties and showed good stability over six months of testing and it attenuates contaminants in the waste leachate.

Soil #3 exhibited good performance with Waste #3 leachate and Waste #4 leachate. The excellent physical barrier provided by this soil's high clay content affords expected reliable field performance.

For future liner studies, the laboratory testing matrix for liner compatibility can be limited to permeability studies which also indicates failure mechanisms, and soil identification for definition of liner properties can be limited to particle size distribution, compaction, Atterberg limits, soil pH, and mineral composition, which provide enough information to properly assess interaction with wastes having similar compositions.

For steel waste-liner studies, the same test matrix will indicate failure mechanisms and identify suitable barriers. Chemical attenuation studies will be necessary in the event that the candidate soil cannot provide an adequate physical barrier.

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Since the information in this document has not been funded, wholly or in part, by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review. Therefore, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

Appendix A

A COMPARTMENTALIZED ONE SLUDGE BIOREACTOR MODEL FOR SIMULTANEOUS ORGANIC AND AMMONIA REMOVAL*

*Published in proceedings only, not presented

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ABSTRACT

The objective of this research is to develop a computer model to simulate toxic inhibition to a single substrate or a series of two or more substrates when at least one of the substrates can also act as a toxicant. The model is based on biokinetics developed earlier with mass balance relationships to demonstrate the effect of inhibition of substrates using a single stage multicompartmented bioreactor. The model is in the process of being further verified by experimental operation of specially designed bench scale reactors for simultaneous or sequential carbonaceous, thiocyanate, and ammonia removal. The results of the matching of nitrification inhibition biokinetics with a reactor model will be a better understanding for design of innovative multicompartmental systems, and upgrading of existing systems to meet BAT limitations for the Iron and Steel Industry.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INTRODUCTION

BAT guidelines for coke plants indicate that while a two-stage (two-sludge) biological process may be used for carbonaceous and nitrogenous removal respectively, it is possible that economical and stable single stage combined systems may be designed for the same application. While this is common for municipal systems, it is uncommon in practice for industrial systems. Understanding of fundamentals for the proper design and operation of single stage systems for nitrification is important for companies that already own and operate such systems as originally constructed to meet BAT phenol effluent limitations, and are now being required to upgrade these facilities to accomodate recent ammonia and phenol effluent limitations.

LITERATURE REVIEW

Several investigators have reported on one stage reactors for nitrification of coke plant wastewaters. Olthof (1) performed treatability studies on coke oven wastewater using a two stage and a one stage system. Wong-Chong and Caruso (2,3) examined a single stage reactor for the treatment of ammonia, free cyanide, phenol and thiocyanate. Wong-Chong and Hall (4) reported on a comprehensive laboratory scale research study of a single stage system for the treatment of coke plant wastewater. The results of this study showed that the single stage system can produce high degrees of treatment, however, the process was sensitive in responding to abrupt changes in feed composition and reactor composition. Jones, et al. (5) also reported on the biological treatment of coke plant wastewater. In their system, treatment of ammonia liquor (influent to the still) appeared to be limited to a TOC of not more than 400 mg/L at a HRT of forty-two hours. The authors state that it is not clear whether the limitation is the inability of the microbes to degrade specific components of the influent, thus increasing the toxicity, or the indirect consequence of filamentous growth that interferes with normal treatment operation. The increase in effluent TOC may cause two different adverse effects. It may result in inhibition of the nitrifying bacteria or it may create a selective environment favoring the development of filamentous bacteria, which may be less sensitive to the increased toxicity. Once these filamentous organisms were established, treatments such as alkaline pH, exposure to hydrogen peroxide, and wasting at 40% or greater did not reduce the filament population.

MODEL DEVELOPMENT

A model was developed and modified from the work of Grady and Lim (6) by application of material balance equations to predict the effluent substrate, biomass in each aeration tank, and the biomass in the clarifier for a compartmentalized bioreactor. The development of the appropriate kinetics is based on the following assumptions:

(1) Complete mixing is achieved in each aeration tank by providing sufficient agitation.

(2) The influent substrate concentration remains constant.

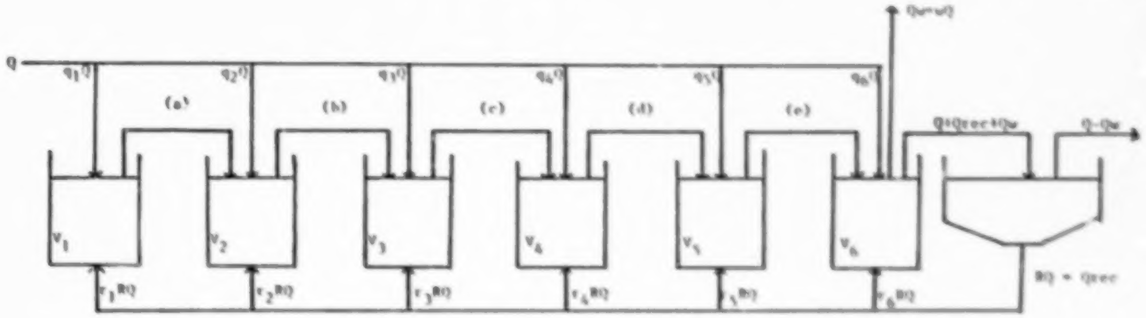
(3) No microbial solids are contained in the raw wastewater fed to the aeration tanks.

(4) All soluble substrate removal occurs in the reactor and none in the clarifier.

(5) All biological activity stops in the clarifier so that no further decay occurs.

Figure 1 illustrates a generalized system which consists of six tanks in series with recycle. The diagram, as well as the model, was derived for the most general situation, meaning that the feed or recycle may enter any or all of the compartments. The feed flows into the aeration tanks at a constant flow rate Q. The fraction of feed entering tank 1 is represented by qi and

$$\Sigma q_i = 1.0 \qquad (1)$$



(a) $(q_1 + r_1R)Q$

(b) $(q_1 + q_2 + r_1R + r_2R)Q$

(c) $(q_1 + q_2 + q_3 + r_1R + r_2R + r_3R)Q$

(d) $(q_1 + q_2 + q_3 + q_4 + r_1R + r_2R + r_3R + r_4R)Q$

(e) $(q_1 + q_2 + q_3 + q_4 + q_5 + r_1R + r_2R + r_3R + r_4R + r_5R)Q$

Figure 1. Flow diagram for 6 compartment bioreactor

The fraction of the recycle flow entering tank 1 is designated r and

$$\Sigma r_i = 1.0 \qquad (2)$$

The aeration tank volume designated as V may or may not be of equal size. Other nomenclature used in the schematic are as follows:

R = recirculation ratio

Q_{rec} = recirculation flow rate = RQ

Q_w = wastage rate = $Q(T/\Theta)$

As shown in the figure, the excess sludge is wasted from the last aeration tank although the research may dictate that the sludge be wasted from the clarifier.

The mass balance model has been developed to predict biomass and substrate concentrations for phenol, thiocyanate, and ammonia for a 1, 2, 3, 4, and 6 compartment system. The biokinetics used in the computation were experimentally determined values based on our prior laboratory research.

The program first calculates the effluent thiocyanate and thiocyanate biomass levels. Then the kinetics for phenol are determined in each compartment by the concentration of thiocyanate in each compartment because thiocyanate concentrations inhibit phenol oxidation. Next, effluent phenol and phenol biomass levels are calculated. The last substrate to be calculated is ammonia taking into consideration the additional ammonia formed in each compartment as a by-product of thiocyanate biodegradation. In addition, the kinetics for ammonia in each compartment are determined by the phenol concentrations. After the kinetics for ammonia are calculated, the effluent ammonia concentrations and biomass levels are determined.

DISCUSSION

Figures 2 through 5 illustrate the effluent substrate concentrations for the different multicompartmented reactors of equal total volume as calculated from the mass balance model. The influent for this comparison is 450 mg/L phenol, 300 mg/L thiocyanate, and 300 mg/L ammonia. The sludge age for these plots is eight days and the hydraulic detention time is one day. Figure 2 shows that a one compartment reactor will produce an effluent containing 0.15 mg/L phenol, 8.50 mg/L SCN, and 4.9 mg/L ammonia. Examination of Figure 3 points out the fact that the effluent phenol, SCN, and NH_3 are much lower in the second compartment than in the one compartment case. For a two compartment system, the reactor effluent phenol concentration will be in the microgram per liter range, while the thiocyanate and ammonia would be equal to approximately 3.0 and 1.5 mg/L respectively. Figure 4 illustrates that for a three compartment system the effluent substrate in the third compartment will be no greater than 1.0 mg/L. Figure 5 shows the effluent substrate concentration for each compartment for a four compartment bioreactor. Figure 5 demonstrates the fact that there is no significant benefit in utilizing four compartments because a three compartment reactor is capable of producing an effluent containing no greater than 1.0 mg/L thiocyanate and ammonia. The additional compartment for the four compartment reactor just results in higher effluent substrate levels in the first three compartments compared to a three compartment reactor with the final reactor effluent for thiocyanate and ammonia equal to less than 0.5 mg/L. Another important point that these figures illustrate is the fact that phenol is degraded first and that the ammonia level can not be reduced until the thiocyanate level is reduced.

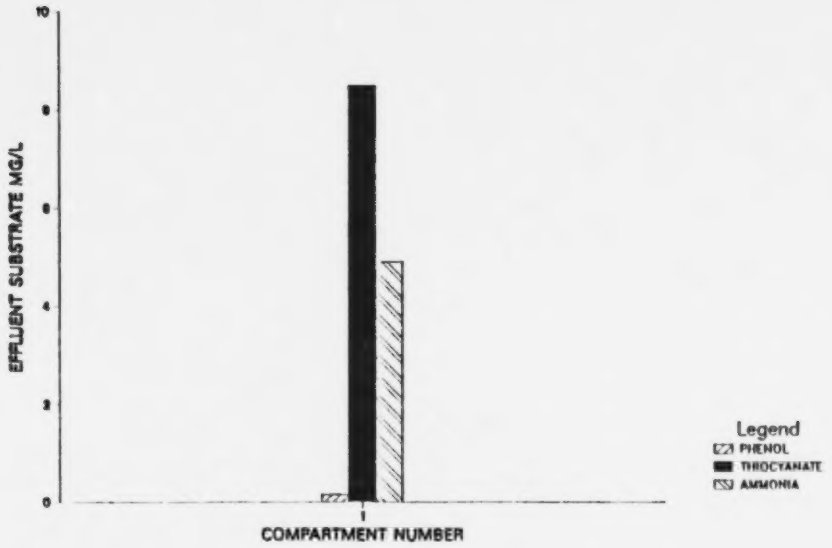


Figure 2. One compartment bioreactor

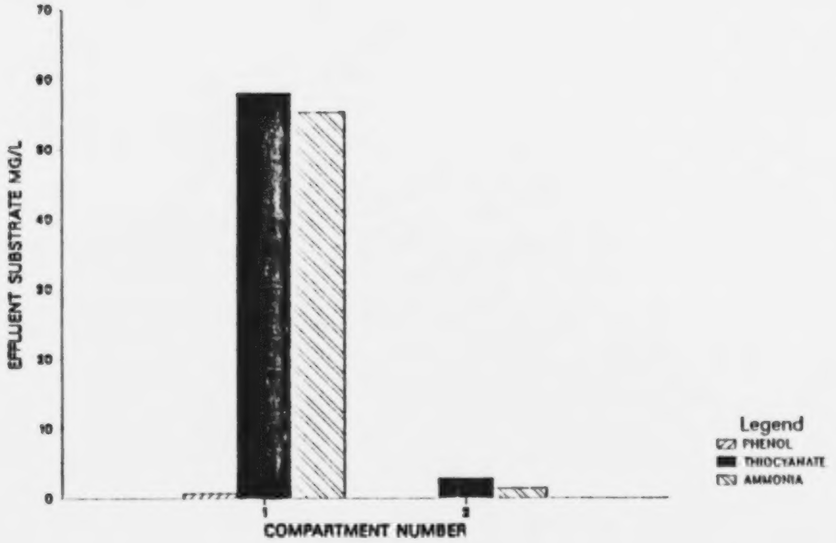


Figure 3. Two compartment bioreactor

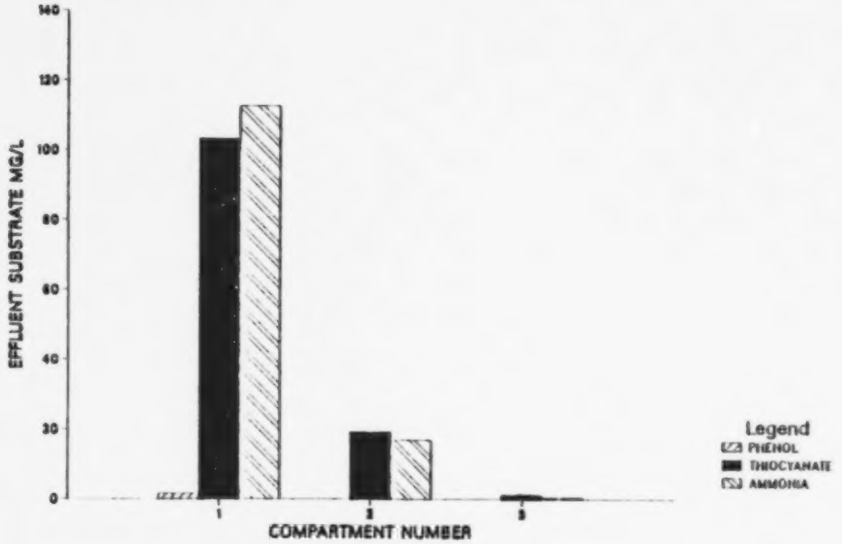


Figure 4. Three compartment bioreactor

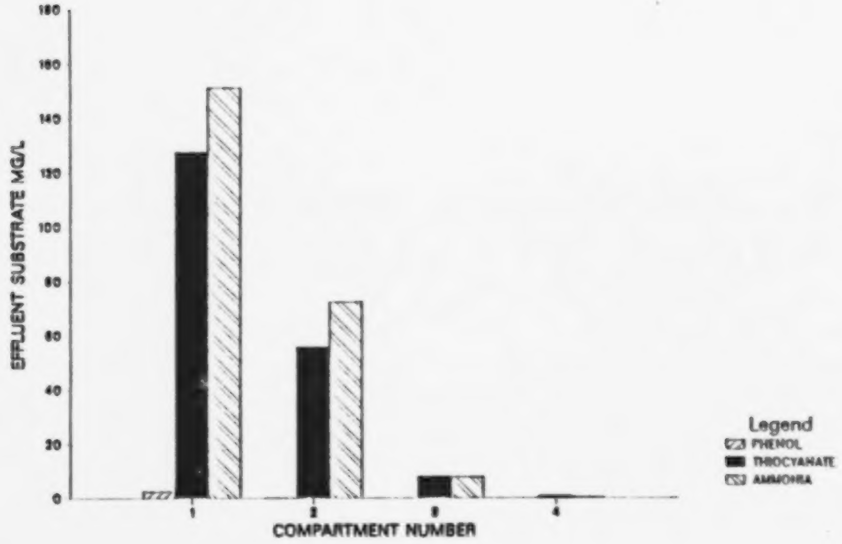


Figure 5. Four compartment bioreactor

Computer similation has also been performed using the same conditions as in the previous diagrams but a comparison was made between different volume configurations for a three compartment reactor. Figures 6 through 8 illustrate the effect of different volume configurations for the compartment volumes representing 20%, 20% and 60% of the total reactor working volume. The best volume arrangement is a three compartment reactor with the first compartment comprising 60% of the total reactor volume. The effluent substrate concentrations for this reactor are shown in Figure 6. Figure 7 illustrates the substrate concentrations for a reactor with the last compartment comprising 60% of the total volume. This reactor produces an effluent in the second compartment with a relatively high SCN concentration which causes the final effluent ammonia concentration to be approximately 4.0 mg/L. Figure 8 demonstrates the configurations where the middle compartment comprises 60% of the total reactor volume. Comparison of Figure 8 and Figure 7 shows that the effluent substrate concentrations are approximately equal in the first compartment but the configuration in Figure 8 has the capability of producing a lower thiocyanate concentration in the second compartment due to the increase in the volume over that of the configuration shown in Figure 7. Therefore, the configuration with a middle compartment of 60% is capable of producing an effluent ammonia concentration less than that of a reactor with the last compartment comprising 60% of the total reactor volume.

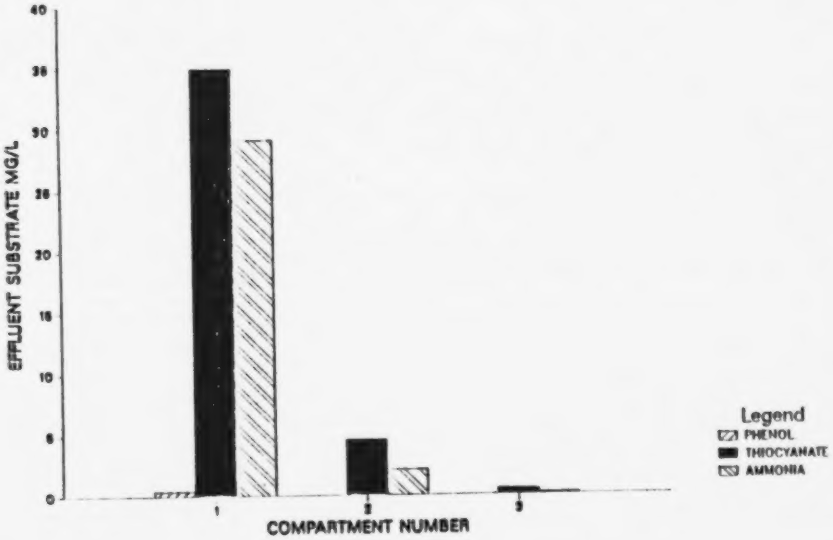


Figure 6. Volume configuration - 60%, 20%, 20%

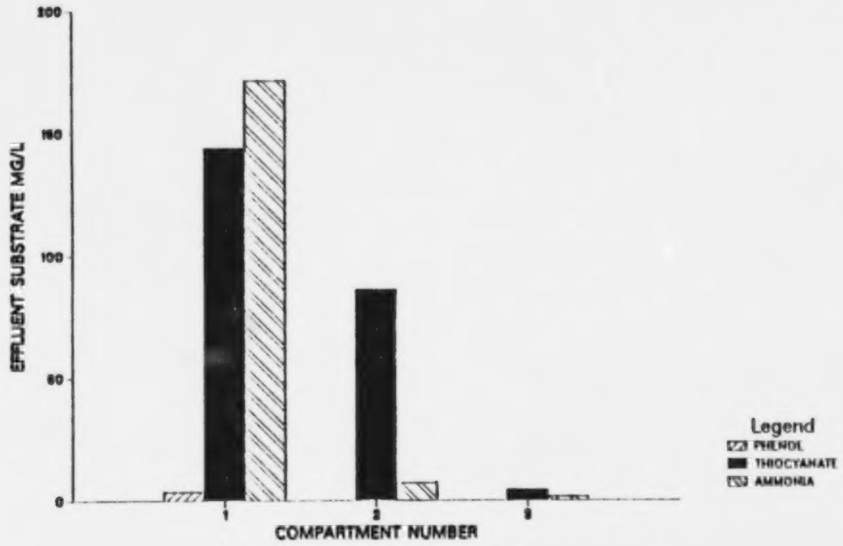


Figure 7. Volume configuration - 20%, 20%, 60%

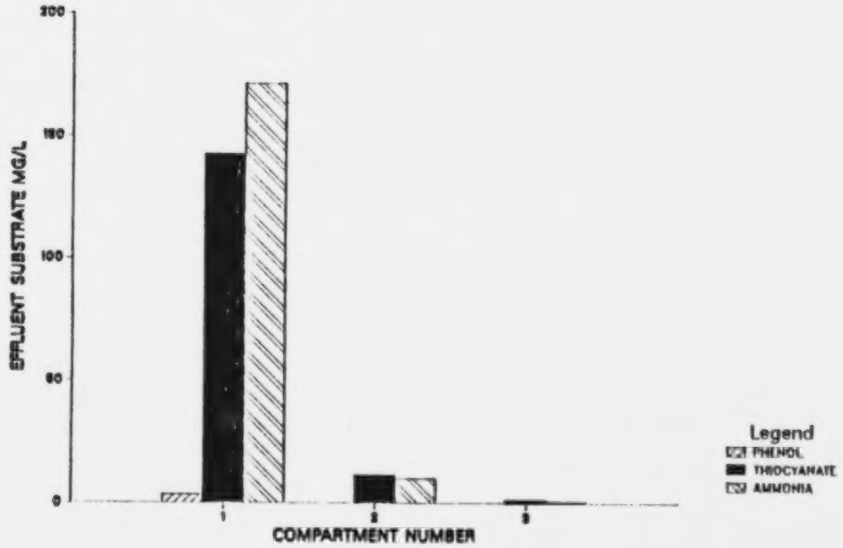


Figure 8. Volume configuration - 20%, 60%, 20%

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